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Evaluation and Selection of Models for Estimating Air Emissions from Hazardous Waste Treatment, Storage, and Disposal Facilities

GCA Corp., Bedford, MA

Prepared for

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The purpose of this report is to provide a source of current information available on this subject area. A guidance manual of practice will ultimately be prepared to assist regulatory engineers and others in applying the recommended models. Since many new papers in this area are continually being published, this selection of modeling techniques may be considered present state-of-the-art as of spring 1983. Field validation scheduled to be conducted in 1983 and 1984 under EPA and private directives should provide additional information regarding model precision.

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Office of Air Quality Planning and Standards
Emission Standards and Engineering Division
Research Triangle Park, North Carolina 27711

December 1984

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Mathematical models describing the release rate of volatile air emissions from hazardous waste treatment, storage and disposal facilities were compiled and reviewed. Mathematical modeling techniques which predict volatile air emissions release rates from landfills, landfarms, surface impoundments, storage tanks, wastewater treatment processes, and drum handling and storage facilities were assessed. Existing field test validation efforts were also reviewed.

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SPECIAL NOTE

A Draft Final Report (October 1982) and a Revised Draft Final Report (May 1983) previously developed for this project were prepared and furnished to U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response (OSWER), Land Disposal Branch under Contract No. 68-02-3168 (Technical Service Area 3, Assignment No. 77). Ms. Alice C. Gagnon served as EPA Project Officer and Dr. Seong T. Hwang of EPA/OSWER served as Task Officer for these efforts. On December 23, 1983, hazardous waste treatment, storage, and disposal facility (TSDF) area source emissions regulatory development was transferred from OSWER to the Office of Air Quality Planning and Standards (OAQPS). This Final Report was prepared under the direction of EPA/OAQPS Task Officer Kent C. Hustvedt in partial fulfillment of Contract No. 68-01-6871, Assignment No. 37.

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SECTION 1

INTRODUCTION

BACKGROUND AND PURPOSE

Under contract with EPA's Office of Solid Waste (OSW), GCA reviewed and evaluated available mathematical models describing the release rate (i.e. mass flux) of volatile air emissions from hazardous waste treatment, storage and disposal facilities (TSDFs). Air emission release rate (AERR) models judged most suitable for estimating air emissions from TSDFs are identified herein along with the rationale for each model selection. Other models available in the technical literature are also described with an indication of their limitations.

The purpose of this report is to provide a source of information for all air emissions release rate models available in the literature. Information contained in this report incorporates comments made by the peer review group in January 1983, and the EPA Task Officer. Since AERR models for TSDFs are continually undergoing development and refinement, and since little field validation data are available, this document presents the best available models as of early 1983.

PROJECT SCOPE AND TECHNICAL APPROACH

Technical efforts were initially limited to an evaluation of existing AERR models reported in the technical literature. A computer-assisted literature search generated 30 references that appeared suitable for review. Additional references became evident as the initial 30 technical articles were evaluated. Telephone surveys were performed to solicit additional information from EPA personnel, active researchers, other EPA contractors, and trade associations such as the American Petroleum Institute and the Chemical Manufacturers Association. A list of the technical references reviewed for this report appears in Appendix A.

On OSW's request, AERR models were investigated for the following TSDF categories:

- Landfills;
- Landfarms (land treatment);
- Surface impoundments;

- Storage tanks;
- Drum handling and storage;
- Treatment units;
- Waste piles (particulate emissions only).*

Treatment units were segregated at the suggestion of OSW into three generic types: (1) open tanks with quiescent surface conditions; (2) open tanks with mixing; and (3) closed-loop treatment units. This approach was developed in order to reduce the large number of treatment unit processes into a manageable size for analysis.

No models were found to describe air emissions from drum handling and storage facilities, although estimates of air emissions can be performed for known spill quantities using appropriate techniques described later in this report. GCA developed a general approach to describe the potential air emissions based on estimates of the fractional loss due to accidental spills.

Some effort was devoted to developing criteria for selecting AERR models most suitable to fulfilling EPA objectives for AERR estimations, and to provide a uniform basis for comparing different models. These efforts were terminated when it became apparent that only a limited number of models were available, and many models had serious limitations. In some cases, only one model was available to describe a particular type of TSDF. Consequently, the following basic criteria were used for model selection:

- Emission release phenomenon actually occurring at a TSDF must be accurately described by the models;
- Input data must be readily obtainable by an Agency engineer either through published literature or calculation techniques easily understood;
- Models must be suitable for use by entry level regulatory engineers with appropriate guidance through a manual.

Section 2 presents the AERR modeling approaches recommended by GCA based on the review and evaluation of current research. Rationale for each selection are also identified. Sections 4 through 8 discuss all AERR models available for each TSDF-type, indicating deficiencies and the rationale for not recommending certain models. The status of AERR Model validation efforts via laboratory and field measurements is provided in Section 3.

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*All other models address volatile air emissions.

Section 9 presents the general approach developed by GCA to describe AERR for drum storage and handling facilities. Section 10 describes methods for quantifying particulate emissions from storage piles. The remainder of this introductory section provides a cursory review of the technical background and discusses the mass transfer principles that form the basis for virtually all AERR models.

TECHNICAL INTRODUCTION

Background

Air emissions of volatile hazardous compounds from TSDFs can enter the atmosphere in two ways: (1) as the result of forced bulk motion on a macroscopic scale; or (2) as the result of diffusion on a molecular or turbulent scale. Examples of forced motion include:

- vapor losses during filling of a storage tank;
- vapor movement in a tank or landfill cell due to pressure gradients created by changes in atmospheric pressure;
- convection due to biogenic gas production in landfills.

Air emissions resulting from forced motions described above do not depend on the volatility of the compound; all molecules simply partake in the macroscopic scale gas motion.

Diffusion of volatile air emissions from a TSDF can generally be thought of in terms of escape of material through multiple layers, with the last layer being the lower atmosphere. For example, as illustrated in Figure 1, nonturbulent diffusive transport in a lagoon proceeds through four stages starting with the bulk liquid, to a laminar liquid layer at the liquid surface, and then through a similar laminar air layer, and finally, into the atmosphere. The rate of transfer (diffusion) through all layers, combined, determines the release rate to the atmosphere. This transfer rate is expressed in terms of the mass transfer coefficient, as will be described later. A compound's volatility, characterized by its solubility, partial pressure, Henry's law constant and diffusivity, provides an indication of the quantity of material in the gas phase which will be subjected to the transfer process. Additionally, turbulence in any of the layers can significantly increase the transfer rate.

Generally, transfer rates in one or perhaps two of several layers will be so low (due to the high resistance in these layers) that these layers will control the overall atmospheric emission release rate. In the example given for a lagoon, the laminar air or liquid phase (or both for some compounds) will control the overall transfer rate.

Similarly, in discussing volatile liquids in landfills, it is possible to describe the process as one of diffusion from bulk waste, through a wetted soil region, through dry soil and into a laminar air layer. However, for any

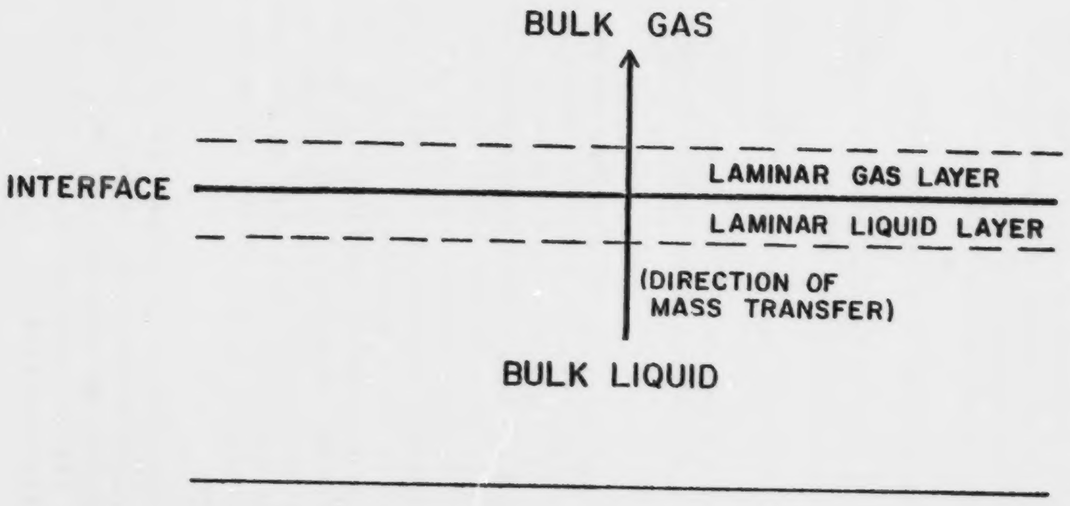
BULK GAS
INTERFACE
LAMINAR GAS LAYER
LAMINAR LIQUID LAYER
(DIRECTION OF
MASS TRANSFER)
BULK LIQUID

Figure 1. Nonturbulent two-layer model of mass transfer.

significant burial depth, diffusion of vapors through the overburden of dry soil will be the most significant factor because the transfer coefficient in soil will be small. Figure 2 shows the probable controlling layer or layers for different TSDFs.

For an open landfill, precisely which layer will control the overall release rate will depend on the specific compound of interest and whether, for example, compounds placed initially on the surface have seeped deeply into the soil.

	SOIL	LIQUID	AIR
LAGOON		X	X
BURIAL (LANDFILL)	X	X	
LAND FARM	X	X	X
SPILL ON IMPERMEABLE SURFACE		X[a]	X
SURFACE DUMP	X		X
STORAGE TANKS		X[a]	X

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[a] Liquid phase controlling for dilute aqueous or hydrocarbon mixtures.

Figure 2. Controlling layer for diffusion losses from different TSDFs.

All state-of-the-art AERR models reviewed were based on mass transfer principles. Whenever the concentration of a chemical or compound varies between two regions there is a natural tendency for mass to be transferred across the interface, and approach equilibrium within the system. Each AERR model reviewed was based on the following relationship which describes diffusion transport across a series of different layers:

Mass flux = (overall mass transfer coefficient) (driving force);

where:

Mass flux = net quantity of material transferred across a unit area normal to the surface in a given unit of time (i.e., grams of a chemical transferred across one square centimeter of an air-liquid interface in one second);

Overall mass transfer coefficient (K) = overall rate of chemical transfer. The reciprocal of the overall K value* is equal to the sum of the reciprocals of individual k-values for each region. Changes in state (liquid-gas) modify this relationship slightly as described below. The reciprocal of the K-value is thus defined as the overall resistance to diffusion. The overall mass transfer coefficient represents the extent of contribution to mass transfer in each region which the chemical must pass through;

Driving force = the differences in chemical potential (i.e., chemical concentration) of the compounds of interest on each side of the boundary between two regions.

The choice of the most accurate model to represent AERR at TSDFs reduces to the problem of finding the "best" individual mass transfer coefficient, k, in each of the regions (soil, liquid, air). The overall mass transfer will, in turn, have a coefficient in the form of a series resistance, $\frac{1}{K} = \sum_i \frac{1}{\alpha_i k_i}$ where K is the overall transfer rate, and α_i is the equilibrium concentration ratio in each boundary layer relative to the layer below. For example, at a liquid-gas interface, α_i is essentially the Henry's Law constant (H_i) divided by the gas constant R and absolute temperature T. For many compounds, H_i has been experimentally determined, or can be calculated from other chemical properties (vapor pressure and solubility).

General Discussion of Available Models

Figure 3 shows for each major reference article investigated during this study the interface or layer which was considered by the respective researcher(s). In Figure 3, note that an "x" to one side of a specific interface indicates that side was considered implicitly to be controlling the overall transfer rate. Figure 3 also shows which forced motions, if any, were treated by various authors.

The substantial difference between each available model is the method employed to calculate the individual mass transfer coefficients (k-values). However, there are also differences in basic assumptions between models. In some cases, assumptions inherent to certain models do not accurately reflect the physical phenomenon responsible for air emissions from TSDFs.

Some authors make assumptions which are inappropriate for our purposes as to which region controls. For example, McCord (1981) bases his approach to non-aerated lagoons on the theory of water evaporation, where the evaporation rate of water is gas phase controlled. However, for most volatile compounds,

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*In this report, a capital letter K refers to the overall mass transfer coefficient and a lower case k refers to the individual phase mass transfer coefficients.

Reference	Forced Emissions	Interface Problems[a]			
		Soil - Air	Liquid - Soil	Liquid - Air	Other Interface
1. Mackay & Leinonen ES&T'75				x	
2. Thibodeaux Parker & Heck AIChE'81				x	
3. Smith, Bomberger & Haynes EST'80				x	Liquid - Surfactant - Air
4. Smith, Bomberger & Haynes, Chemosphere'81				x	
5. Shen, JAPCA, '82				x	
6. Hwang Env. Prog.'82		x	x	x	
7. Thibodeaux, Hwang Env. Prog.'82		x	x		
8. McCord Haz. Waste Conf.'81				x	
9. Hartley Pesticide, '69				x	
10. Shen, APCA'80		x			
11. Steenhuis, Bubenger & Converse, ASAE'79		x			
12. Thibodeaux, J. Haz. Mat.'81		x			
13. Farmer, Yang, Letey, 1978, 1980		x			

Figure 3. Interface problems investigated by respective researchers for treatment and disposal AERR models. (A complete list of references is provided in Appendix A.)

Reference	Forced Emissions	Interface Problems[a]			
		Soil - Air	Liquid - Soil	Liquid - Air	Other Interface
14. Thibodeaux Springer & Riley, 1981	x	x			
15. Liss & Slater, Nature'74				x	
16. Mackay, Haz. Assess. of Chem.'81				x	
17. Owens, Edwards, Gibbs, Int. J. Air, Water Poll.'64				x	
18. Neely, Dow Chemical, 1976				x	
19. Dilling, Tefertiller, Kallos EST'75				x	
20. Dilling EST'77				x	
21. Mackay & Yuen Water Pol Journal Canada'80				x	
22. Arnold Trans of Am. Inst. Chem., 1944				x	
23. Cohen, Cocchio, MacKay EST'78				x	
24. Mackay, Matsugu Canadian Journal'73				x	
25. Mackay, Wolkoff, '73				x	
26. Thibodeaux, Springer Hedden & Lunney, 1982				x	

[a] x denotes the authors interpretation of which phase(s) control the overall transfer rate.

Figure 3 (continued)

especially low solubility organics, the liquid phase controls the overall diffusion rate. As another example, Hartley's (1969) land disposal model is actually most appropriate for lagoons or compounds spread on an impermeable surface. Since the Hartley model does not address diffusion in soil, but only in air, it is not appropriate when wastes are plowed or percolate into the ground.

The principle requirement in selecting the most appropriate k-value (and model) is that it embody the correct mass transfer principles. This does not necessarily assure accuracy, but it does provide a good foundation for model refinements. The mass transfer coefficient in air, for example, is determined by the vertical wind speed profile and turbulence structure in the earth's boundary layer. All references examined which recognize this fact follow the original formulation by Sutton (1953). Diffusion in air-filled spaces within the ground, however, occurs on a molecular level, thus the soil k-value depends primarily on the soil porosity and geometry. The problem is thus one of describing the available "space" within which diffusion occurs. Finally, at the liquid side of an interface, k-value determinations have been obtained mainly in the laboratory. Although laboratory-developed correlations describing k-values are available for both aerated and unaerated surfaces, no extensive data presently exists that places adequate confidence on extrapolating these correlations to field conditions.

The next section summarizes GCA's preliminary model selections for each TSDF category. Later sections provide a more complete literature review describing each available model in more detail.

SECTION 2

SUMMARY AND CONCLUSIONS

INTRODUCTION

The mechanisms causing air emissions of volatile compounds from TSDFs were briefly described in the introduction. The basis for quantifying air emission release rates (AERR) begins with an accurate description of diffusion across different regions in a TSDF; i.e., the diffusive transport of air emissions across soil, liquid and/or air layers.

Diffusive transport can be quantified by determining the mass transfer coefficient ("k-value") for each region encountered by the potential air emission. Selecting the most appropriate AERR model for TSDFs reduces to a problem of selecting the most accurate and manageable k-value. Once the best technique for determining k-values is established for each type of diffusive transport occurring, the model that most accurately describes the physical situation at a TSDF can be selected.

This section summarizes techniques available in the literature for determining individual k-values*, and presents GCA's recommendations for AERR models based upon our selected k-values. When applicable, recommended model approaches are presented. Later sections of the report discuss models in more detail.

It should be noted that the majority of the k-value correlations presented in this report have not undergone substantial field test validation or verification. For the most part, k-values were developed from laboratory experimentation and some limited field studies. Therefore, caution is advised when applying these correlations to calculate expected emission release rates. Although limited field validation has been performed recently, the accuracy of all emission release rate models is still unknown.

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*In this report, a lower-case letter k refers to the individual mass transfer coefficients for each region; an upper-case K refers to the overall mass transfer coefficient obtained from the individual k-values.

AVAILABILITY AND SELECTION OF MASS TRANSFER COEFFICIENTS (k-VALUES)

Several researchers have developed empirical relationships to describe the mass transfer of contaminants from individual regions or phases, i.e., through soil, liquid and air. These mass transfer coefficients can be categorized according to their applicability to TSDFs as follows:

- Soil (k_{soil})--describes molecular diffusion in porous media; i.e., landfarms and landfills;
- Liquid (k_{liquid})--(a) molecular mass transfer (diffusion) within a stagnant liquid; (b) turbulent diffusion from the surface of a liquid (impoundment) affected by wind; and (c) turbulent diffusion enhanced by mechanical aeration;
- Gas (k_{gas})--(a) turbulent diffusion influenced by wind, and (b) turbulent diffusion enhanced by mechanical aeration.

Table 1 presents the individual mass transfer coefficients available from the literature reviewed by GCA for each region. When more than one technique for determining the k-value was available in the literature, GCA's recommendation of the most appropriate k-value is noted with an asterisk (*). Only one technique was available for quantifying the individual liquid and gas phase k-values for agitated conditions. Likewise, simplification techniques found in the literature are not shown in Table 1, since these techniques provide methods to simplify the calculational effort involved, and do not represent different approaches to determining k-values. The simplification techniques are presented later in this report.

The following discussions review in detail all available k-value relationships shown in Table 1, and describe the theoretical basis used by GCA in selecting the most appropriate equation for AERR estimates.

Soil-Phase Mass Transfer Coefficient (k_{soil}, k_s)

Vapor diffusion through air filled pore spaces in soil is a complex phenomenon which is not amenable to a purely theoretical treatment. To obtain an effective diffusion coefficient for a particular soil at a known moisture content, the problem requires that empirical correlations for vapor diffusion in porous media be evaluated to see if they adequately reflect the many experimental observations which are available. GCA has reviewed these correlations for simple systems such as dry sands and for some more complex systems such as platey minerals and soils of known moisture content. With presently available data, it should be possible to provide first order estimates of effective diffusion coefficients. GCA's evaluation of these data is summarized below.

In order to model AERR from landfills and landfarms, vapor movement within the soil must be accurately defined. Farmer et al. (1978) and Thibodeaux (1981a) have both defined the "effective" diffusion coefficient within soil as a function of the volatile components' molecular diffusivity and the physical characteristics of the respective soil.

TABLE 1. MASSS TRANSFER COEFFICIENTS (k's) AVAILABLE IN THE LITERATURE APPLICABLE TO MODELING TSDF AIR EMISSION RATES (SEE TEXT FOR TERM DEFINITIONS)

Transfer phase	Transfer coefficient (k)	Author (date)	Comments
1. **Soil** (k_{soil}, k_s)	$D_a \frac{\epsilon_a^{10/3}/\epsilon_T^{2}}{h}$	Farmer (1978)	• Based on work by Millington and Quirk (19 describing the effects of soil water content on vapor movement.
	$\frac{D_a \epsilon}{\lambda h}$	Thibodeaux (1981a)	• Based on the theory of molecular movement in porous media but defines only dry-soil phase.
	More general ε power law models	Currie (1960, 1961)[a] and others	• See text.
2. **Liquid** (k_{liquid}, k_L) -			
a. Molecular Diffusion-- Quiescent State	$\frac{D}{h}$	----	• Based on Fick's first law; of limited usefulness in TSDF problems.
b. Turbulent Diffusion-- Wind Effects	$(11.4\, R_e^{*\,0.195} - 5.0)$	Cohen, et al. (1978)	• Based on laboratory wind wave tank studies for hydrocarbon volatilization from aqueous solutions. Lab studies may not fully represent actual environmental conditions.
	$\sim D_L^{0.5}$; from k_l vs. wind speed	Mackay (1981)[a]	• Based on solution of Fick's second law and critical review of existing data (postulating reasonable values for k_L as function of wind speed).
	$3.12\,(1.024)^{\theta-20}\,U_o^{0.67}\,H_o^{-0.85}\left(\frac{D_{i,H_2O}}{D_{O_2,H_2O}}\right)$	Hwang (1982) from Owens, et al. (1964)[a]	• Developed from theoretical, experimental and field measurements of oxygen reaeration rates from flowing streams.
c. Turbulent Diffusion-- Aeration Effects	$\frac{J(POWR)\,(1.024)^{\theta-20}\,(\alpha)\,(10^6)}{165.04(a_v)\,(V)}\left(\frac{D_{i,H_2O}}{D_{O_2,H_2O}}\right)^{0.5}$	Thibodeaux (1978)[a]	• Developed from research on the absorption of oxygen into water during agitation.
3. **Gas** (k_{gas}, k_G)			
a. Turbulent Diffusion-- Wind Effects	$0.0292\, U_{air}^{0.78}\, X^{-0.11}\, Sc^{-0.67}$	Mackay and Matsugu (1973)[a]	• Based on work of Sutton, and field measurements on the evaporation of organic compounds and water into air.
	$0.03\left(\frac{D_{i,air}}{D_{H_2O,air}}\right)U_8\, A^{-0.05}$	Thibodeaux and Parker (1974) from Harbeck (1962)	• Based on field measurements from the evaporation of water into the air.
b. Turbulent Diffusion-- Aeration Effects	$0.00039\,\frac{\rho_g D_{i,air}}{d}\,(N_{Re})^{1.42}(N_{FR})^{-0.21}(N_p)^{0.4}(N_{Sc})^{0.5}$	Reinhardt (1977), as presented by Hwang (1982)[a]	• Based on preliminary experimental investigations for liquid spherical droplets ejected into a gas phase.

[a] Denotes GCA's recommendation.

Pore diffusion, as related to the soil matrix, occurs by the Fick diffusion mechanism. Within the soil matrix, the effective area for transport is less than that for uniform pore structures because the diffusion paths are irregularly shaped channels. Increases in soil moisture will reduce the air-filled porosity and at the same time increase the diffusion path length. Therefore, the mass flux for soil-phase diffusion needs to be described in terms of an "effective" diffusion coefficient which is less than the molecular diffusion coefficient and dependent upon variables influencing the diffusing vapor; i.e., moisture content.

The effective diffusion coefficient presented by Farmer (1978) was formulated from theoretical soil hydraulic conductivity studies of Millington and Quirk (1961). Based on a theoretical derivation, Millington and Quirk presented the following correlation for the effective vapor diffusion coefficient:

$$\frac{D_e}{D_o} = \frac{\varepsilon_a^{10/3}}{\varepsilon_T^2}$$

where: D_e = effective diffusion coefficient in soil;

D_o = air diffusion coefficient;

ε_a = air-filled porosity;

ε_T = total porosity.

For dry soil, when $\varepsilon_a = \varepsilon_T$, this expression reduces to the following:

$$\frac{D_e}{D_o} = \varepsilon_T^{1.33}$$

However, an additional literature review of vapor diffusion in porous media conducted by GCA indicates that the Millington and Quirk correlation is limited to a specific soil type. Further, the Millington and Quirk analysis cannot be of general applicability to the diffusion problem when pores of different sizes are present. In diffusion, flux is proportional to pore radius squared. In hydraulic flow, flux is proportional to pore radius to the fourth power.

In one particularly relevant study, Currie (1960) conducted hydrogen diffusion experiments with 15 different types of dry porous media and concluded that the primary influences on the D_e/D_o ratio were porosity, and particle shape. Differences in particle shape affect the diffusion path. Therefore, the effective diffusion coefficient in porous media is a function of internal geometry and porosity.

The empirical equation proposed by Currie was of the form:

$$\frac{D_e}{D_o} = \gamma \varepsilon^{\mu}$$

where γ and μ are constants for a specific type of porous material. Figure 4 is a log-log plot of D_e/D_o versus ε developed by Currie. Figure 4 shows that the set of data points for a given material lie on a straight line, but the slope of the line (value of μ) varies with each type of material. The following values of μ were determined from the data on dry soils:

Soil Type	μ
Solid grains (i.e., sand)	1.4
Soil crumbs	1.7
Kaolin (a type of clay)	2.6
Platey minerals (mica, vermiculite)	11.0

The value of γ has been found to range from 0.8 to 1.0 for the materials tested. Thus, an equation with two empirical constants (γ and μ) is available to describe the affect of soil porosity (ε) on the effective diffusion coefficient (D_e) for vapors in dry soil.

Limited data are available for describing the effect of moisture content on the effective diffusion coefficient in wet soils. Currie (1961) examined the effect of moisture on some granular materials, and his data fit the following empirical equation:

$$\frac{D_e}{D_o} = \gamma\ (\varepsilon_T)^{\mu-\sigma}\ (\varepsilon_a)^{\sigma}$$

where: ε_T = total porosity;

ε_a = air-filled porosity;

$\sigma \cong 4$ for granular materials subjected to moisture testing.

This correlation is obtained by combining Currie's dry soil and wet soil correlations. The complete derivation is provided in Appendix B.

Currie's empirical formula relating D_e to soil parameters accounts for experimental observations for all soils tested. The formula allows one to define D_e at any specified moisture content provided that the required parameters can be experimentally evaluated. Taylor (1949), Rolston and Brown (1976), Lai et al. (1976), and Ball et al. (1981), also present data for wetted granular soils. Unfortunately clay materials (clayey soils) of the sort expected to be employed for landfill caps have not been tested.

Although it appears that Currie's work provides a solid empirical base and adequate general theoretical interpretation for the effect of particle shape and moisture content on D_e, there are questions concerning the direct application of Currie's results to estimation of volatile organic emissions from landfills. The unsteady state hydrogen diffusion experimentations may

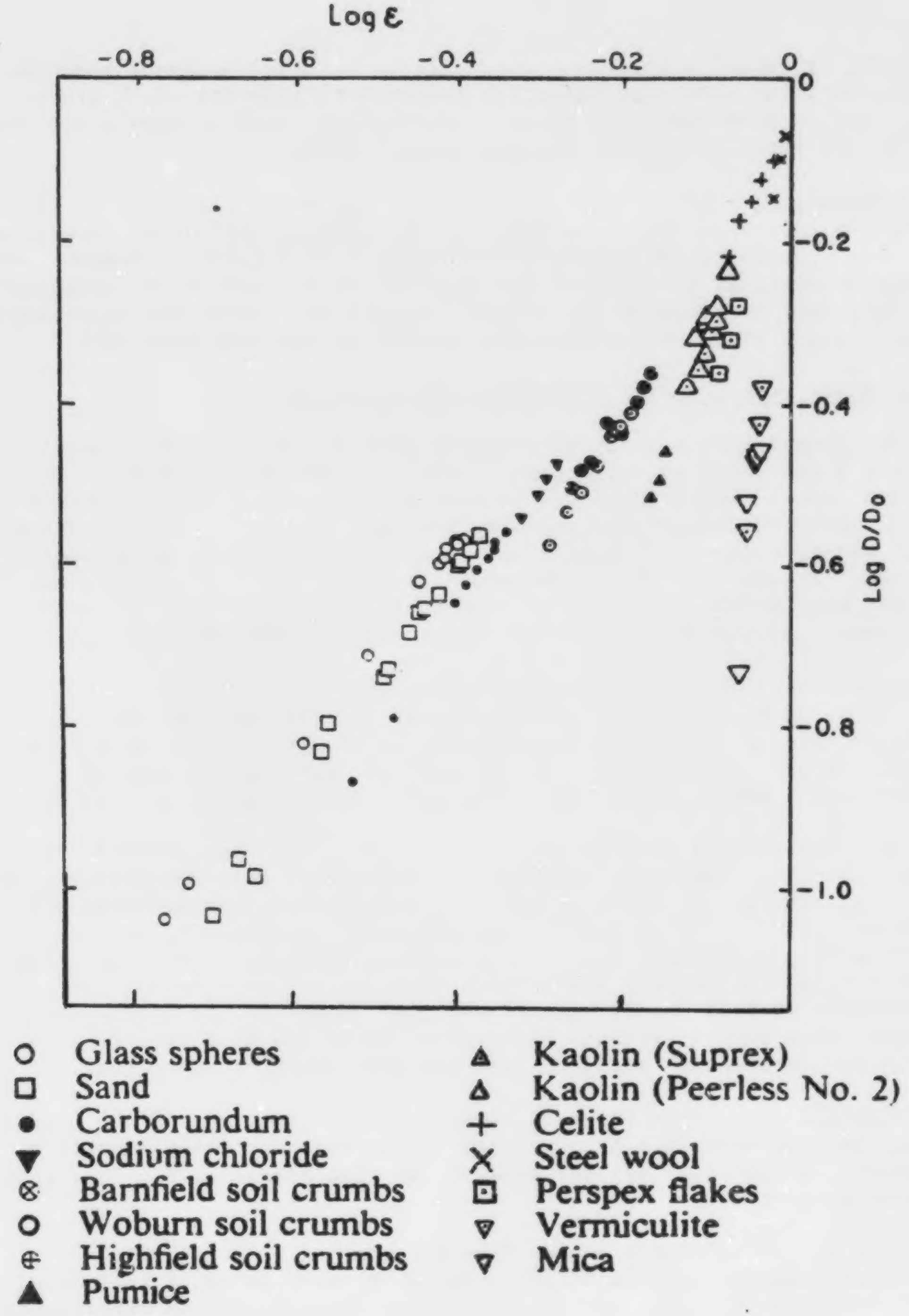

Figure 4. Dependence of coefficient of diffusion on porosity log (D/D_0) versus log ε (from Currie (1960)).

not fully represent a hazardous waste landfill situation since hydrogen is a small, non-polar molecular structure compared to organics which are more bulky, and in some cases are polar. In addition, organic vapors are likely to sorb to the organic material present in most soils.

However, data on vapor diffusion in porous media presented in the literature indicates that determination of effective diffusion coefficient is soil-type dependent. At present, GCA suggests that field validation efforts include an analysis of landfill cap material (i.e., soil type, moisture) such that k_{soil} may be properly quantified. Additional laboratory experimentation for wet soils, especially clays, may provide an improved data base.

Liquid-Phase Mass Transfer Coefficient (k_{liquid}, k_L)

The transfer of a chemical compound within a liquid medium was identified in Table 1 for three specific cases; i.e., (1) molecular diffusion within a stagnant liquid with no wind and no flow effects; (2) diffusion within the liquid-phase enhanced by the turbulence caused by wind; and (3) diffusion within the liquid-phase enhanced by the turbulence created by mechanical aeration. Figure 5 shows the relationship of the six liquid-phase mass transfer coefficient correlations presented in the literature as a function of wind speed. Liquid phase k-values applicable to TSDFs are highlighted.

Molecular Diffusion--k_L for No Wind Conditions--

The first case of liquid diffusion has limited applicability to TSDFs, but is provided for illustrative purposes in Figure 5. This mass transfer coefficient becomes necessary for the case of open tank storage of a multicomponent waste, where wind effects are eliminated by a large freeboard.

The situation of no wind is not too unusual for open areas during evening hours, typically when water temperatures are higher then the surrounding air. Most mass transfer correlations reviewed incorporate wind speed as a parameter, however, it is likely that emissions release will continue under low or no wind conditions due to turbulence created by thermal agitation. Thibodeaux, et al. (1982b) present a method for determining the mass transfer coefficients in both phases (liquid and gas) by use of the Chilton-Colburn analogy. This analogy permits the evaluation of the mass transfer coefficient through the information obtained from the heat transfer phenomenon.

Figure 5 shows that the mass transfer coefficient calculated from this analogy is greater than that predicted by correlations using wind as a parameter, specifically for the case of low wind speeds (i.e., less than 3 meters per second).

Turbulent Diffusion from Wind and Flow Effects--

In the case of turbulent diffusion, where turbulence is influenced by variations in wind speed, several researchers have conducted experiments in order to develop empirical expressions for determining the liquid-phase mass transfer coefficient. The results of these correlations are shown in Table 2.

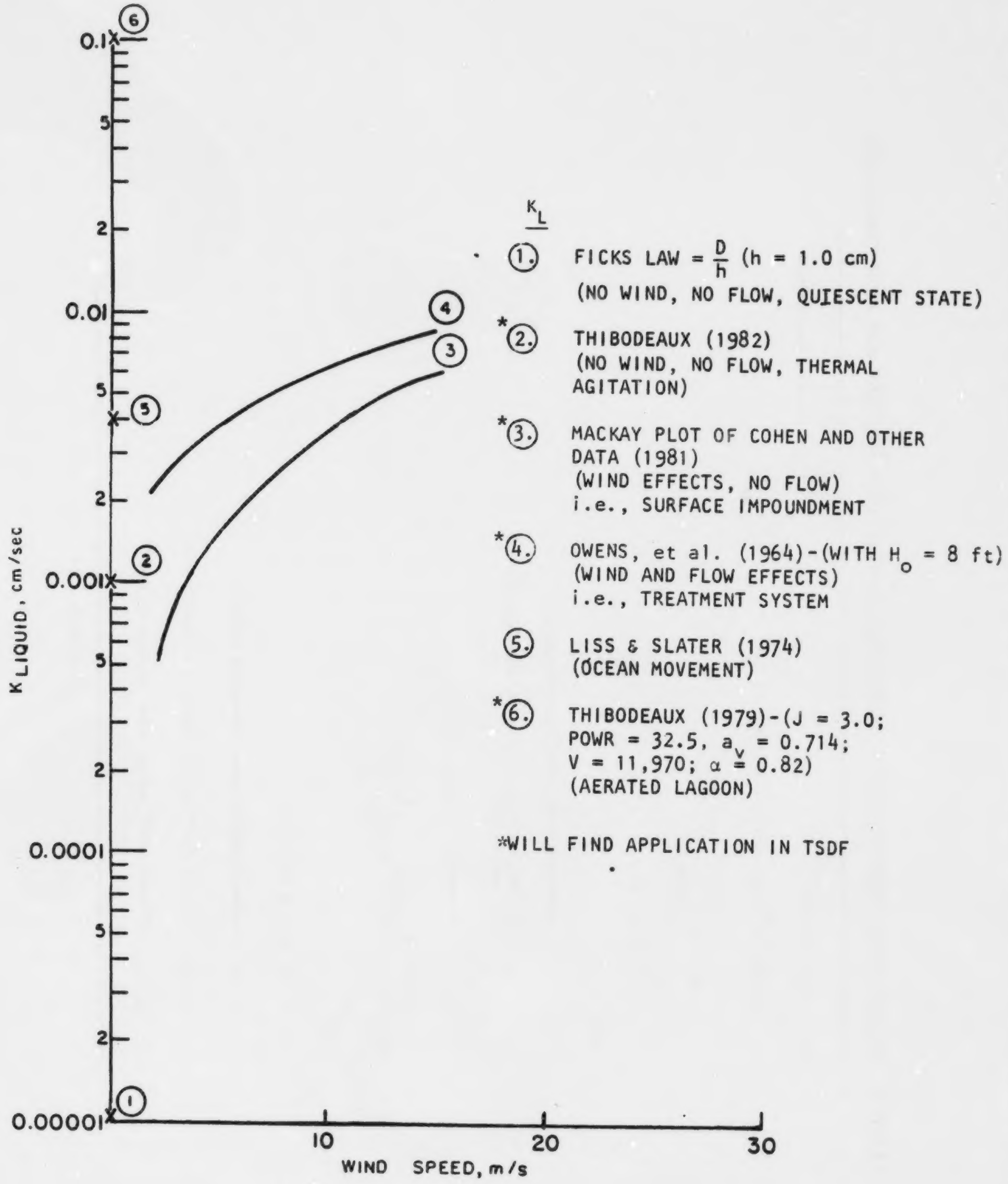

Figure 5. K_L correlations versus wind speed for benzene at 25°C.

TABLE 2. LIQUID-PHASE MASS TRANSFER COEFFICIENT CORRELATIONS FOR WIND AND FLOW TURBULENCE

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[1] $k_L = (11.4\ Re^{*0.195} - 5)$ (Cohen, Cocchio, Mackay, 1978)

for 0.11 $Re^* \leq 102$, where k_L is in cm/hr and

$$Re^* = \frac{7.07 \times 10^{-3}(Z_{10})(U_{10})^{1.25}}{\nu_a \exp(56.6/U_{10}^{0.25})}$$

If $Re^* < 0.11$, then $k_L = 2.4$ cm/hr

where:

Re^* = roughness Reynolds number (dimensionless)

U_{10} = wind velocity (cm/s) measured at height Z_{10} above the water surface (cm)

ν_a = air kinematic viscosity (cm^2/sec)

[2] $k_L = (1.3\ Re^{*0.195} - 0.57)\left(\frac{D_{i,H_2O}}{D_{TOL,H_2O}}\right)$ (Hwang, 1982)

where:

k_L is in lb-mol/ft^2-hr

Re^* = roughness Reynolds number (determined as above)

D_{i,H_2O} = diffusion coefficient of compound i in water (cm^2/sec)

D_{TOL,H_2O} = diffusion coefficient of toluene in water (cm^2/sec)

(continued)

TABLE 2 (continued)

[3a] $k_L = 27.5\ (1.0241)^{\theta-20}\ U^{0.67}\ H^{-0.85}$ (Owens, Edwards, Gibbs, 1964)

where:

k_L is in cm/hr

θ = temperature, °C

U = mean velocity of stream (ft/sec)

H = mean depth of stream (ft)

(valid for the following experimentally observed ranges: $U = 0.1\text{-}5.0$; $H = 0.4\text{-}11.0$)

[3b] $k_L = 29.5\ (1.0241)^{\theta-20}\ U^{0.73}\ H^{-0.75}$ (Owens, Edwards, Gibbs, 1964)

(for fast flowing or shallow streams where $U = 0.1\text{-}1.8$; and $H = 0.4\text{-}2.4$)

[4] $k_L = 3.12(1.024)^{\theta-20} U_o^{\ 0.67} H_o^{\ -0.85} \left(\frac{D_{i,H_2O}}{D_{O_2,H_2O}} \right)$ (Hwang, 1982)

where:

k_L is in lb-mol/ft^2-hr

θ = temperature (°C)

U_o = surface velocity, ft/sec, normally 0.035 x wind speed (ft/sec) for natural surface, and 0.1 ft/sec for outside region of effect of aerators in biological treatment.

H_o = one-half the effective depth of surface impoundment (ft)

D_{O_2,H_2O} = diffusion coefficient of oxygen in water (cm^2/sec)

D_{i,H_2O} = diffusion coefficient of compound i in water (cm^2/sec)

(continued)

TABLE 2 (continued)

[5] $k_L \propto D^{0.5}$ (Mackay, 1981)

from literature data:

Wind speed (m/s)	k_L (m/sec) - for Benzene @ 20°C	
	Environment	Tank
2	5×10^{-6}	10×10^{-6}
5	15×10^{-6}	25×10^{-6}
10	35×10^{-6}	65×10^{-6}
15	60×10^{-6}	100×10^{-6}

The first correlation presented in Table 2 was developed from laboratory wind wave tank studies by Cohen, et al. (1978). Cohen et al. developed their equation for benzene and toluene and indicated k_L dependence on wind speed for velocities between 3 and 10 m/s (6.7 to 22.4 mph). Below 3 m/s, k_L was influenced by subsurface agitation, while at wind speeds above 10 m/s, k_L increased was due to the presence of spray, bubble entrainment and white capping. Cohen expressed concern over the direct application of this correlation to environmental conditions because laboratory tests cannot accurately predict conditions of fully developed flow. That is, the width of Cohen's experimental unit may not simulate a larger surface impoundment at a TSDF.

In applying this correlation to different chemical species, one can refer to three mass transfer theories stated in the literature:

- Stagnant film theory;
- Penetration or surface renewal theories; and
- Boundary layer theory.

The first case identifies k_L as a linear function of diffusivity. However, other theories of mass transfer, namely, those mentioned above in the second case, identify this dependency to the 0.5 power. The third theory is generally considered a compromised approach and identifies the diffusivity dependency to the two-thirds power. The exact dependence of k_L on diffusivity remains to be established.

The second equation shown in Table 2 is a reworking of Cohen's correlation presented by Hwang (1982). The remodeled correlation simply expresses k_L in different units (lb-mol/ft^2-hr). Hwang also suggests a linear dependency to diffusivity.

Equations (3a) and (3b) presented in Table 2 are based on reaeration stream studies discussed by Owens et al. (1964). Unlike the wind velocity dependency analyzed by Cohen, Owens correlations show k_L dependent on stream velocity and water depth.

Although Owens expression suggests hydraulic effects influence k_L, which is in agreement with theoretical models, the direct application of stream coefficients to surface impoundments is questionable since the degree of turbulence offered by a flowing stream is much greater than wind induced turbulence. Thus, Hwang (1982) provides a modification to Owen's correlation to define the surface velocity of water as a function of wind speed (Equation (4) in Table 2). This modification is a more accurate representation of surface impoundment or treatment basin surface actions. Both correlations also show that k_L is dependent upon water depth for a flowing system. Note that Hwang's modification also reflects a change in k_L units (lb-mol/ft^2-hr).

Mackay (1981) critically reviewed the existing data base for k_L determinations, which included laboratory tank experiments and field measurements in lakes. Mackay's data base included the laboratory studies of Cohen, et al. (1978), Liss and Slater (1974), Kanwisher (1963), and Deacon (1977). Field studies of Broecker and Peng (1974), Emerson (1975) and Schwartzenbach, et al. (1974) were also mentioned. Mackay presented what he considered as reasonable values of k_L for environmental and laboratory conditions as a function of wind speed (correlation (5) in Table 2). The data presented in Table 2 are for benzene at 20°C. As stated by Mackay, it appears the best correlating approach for estimating k_L for different chemical species under similar conditions is to use the square root of the diffusivity ratio. Mackay also mentions that there are theoretical reasons suggesting that the ratio of Schmidt numbers to the power -0.5 is the best correcting ratio for both solute diffusivity and temperature. However, he grants no judgment on this statement.

The turbulent k_L correlation selected should be based on the degree to which water is flowing through the system. For nonflow systems, i.e., wind induced flow, k_L as presented by Mackay (1981) appears most appropriate since he compiled data from several researchers. Selecting the Mackay data, or rather the plot of Mackay's data, avoids the calculation of a roughness Reynolds number.

For flowing systems, the correlation presented by Hwang (1982) based on the work of Owens (1964) seems most appropriate. Whereas, Owens turbulent k_L is dependent upon the stream velocity, Hwang's approach considers the effect of the water's surface velocity, which is a function of wind speed. For large impoundments of water where the mean water velocity may be quite low, it is the upper surface layer of water directly affected by wind that will affect k_L the most.

It can be concluded from data presented in the literature, and from theories of mass transfer, that the liquid phase mass transfer coefficient depends somewhat on diffusivity. However, the magnitude of this dependency is not precisely defined by existing research. The mass-transfer coefficient will be proportional to a power of the molecular diffusivity between 0.5 to 1.0, where the lower number represents conditions of high turbulence and the higher number represents near stagnant conditions.

Springer (1983) noted that one aspect of ongoing work at the University of Arkansas involves developing a correlation which employs a dimensionless ratio of fetch to depth. The correlation will be shown to fit data from earlier stream reaeration studies as well as recent experimental work, including the "reasonable values" presented by Mackay (1981).

Turbulent Diffusion from Mechanical Mixing--

The third case of liquid phase mass transfer involves turbulent diffusion created by mechanical aeration. Considerable research has been conducted on scale models and prototype mechanically agitated water surfaces to determine the absorption rate of oxygen. Since oxygen absorption is liquid-phase controlling, the reported values can be transformed to yield a liquid-phase mass transfer coefficient under agitated conditions. The following relationship is the only correlation appearing within the literature:

$$k_L = \frac{J(\text{POWR})(1.024)^{\theta-20}(\alpha)(10^6)}{165.04(a_v)(V)}\left(\frac{D_{i,H_2O}}{D_{O_2,H_2O}}\right)^{0.5} \qquad \text{(Thibodeaux, 1978)}$$

where: k_L is in lb-mol/ft^2-hr;

J = oxygen-transfer rating of mechanical aerator (3 lb O_2/hr-hp);

POWR = total power input to aerators (hp)-rated hp x efficiency (0.65-0.9);

θ = temperature (°C);

α = oxygen-transfer correction factor (0.8-0.85);

a_v = surface area per unit volume of surface impoundment (ft^{-1});

V = volume of surface impoundment in region of effect of aerators (ft^3);

D_{i,H_2O} = diffusion coefficient of compound i in water (cm^2/sec);

D_{O_2,H_2O} = diffusion coefficent of oxygen in water (cm^2/sec).

Gas-Phase Mass Transfer Coefficients (k_{gas}, k_G)

The final mass transfer region that all chemical compounds must encounter is diffusion within the gas phase. As illustrated in Table 1, two cases of gas-phase mass transfer must be considered; i.e., (1) turbulent diffusion influenced by wind speed, and (2) turbulent diffusion created by mechanical aeration.

Turbulent Diffusion from Wind Effects--

A review of the literature revealed two correlations developed from experimental field measurements for determining the influence of wind speed on the gas-phase k-value. These relationships appear in Table 3.

The correlation proposed by Mackay and Matsugu (1973) was developed from experiments on the evaporation of isopropyl benzene (cumene), gasoline and water into air. Their research showed that the work of Sutton (1953), who assumed that the wind velocity profile follows a power law, could be used to quantify the rate of evaporation from a smooth liquid surface, and subsequently obtain an expression for the gas-phase mass transfer coefficient. The final result of Mackay and Matsugu's research provided the correlation shown in Table 3 as a function of wind speed and the effective diameter of the liquid surface.

TABLE 3. GAS PHASE MASS TRANSFER COEFFICIENT CORRELATIONS

[1] $k_G = 0.0292 \; U^{0.78} \; X^{-0.11} \; Sc^{-0.67}$

(Mackay, Matsugu, 1973)

where: k_G is in m/hr

U = wind speed, m/hr

X = effective pool diameter, m

S_c = gas Schmidt number (dimensionless), calculated from:

$$S_c = \mu_g / \rho_g \, D_{i,air}$$

where μ_g is the absolute viscosity of the gas (g/cm sec), ρ_g is the density of the gas (g/cm^3), and $D_{i,air}$ is the molecular diffusivity of compound i in air (cm^2/sec).

[2] $k_G = 0.03 \left(\frac{D_{i,air}}{D_{H_2O,air}} \right) V_8 \; A^{-0.05}$

(Harbeck, 1962; as presented by Thibodeaux and Parker, 1974)

where: k_G = individual gas phase mass transfer coefficient (lb-mol/ft^2-hr)

$D_{i,air}$ = molecular diffusivity of compound i in air (cm^2/sec)

$D_{H_2O,air}$ = molecular diffusivity of water vapor in air (cm^2/sec)

V_8 = wind velocity measured at 8m above the water surface (miles per hour)

A = surface area of the impoundment (acres)

Hwang (1982) modified the Mackay/Matsugu correlation to reflect a change in k_G units (lb-mol/ft^2-hr). The modification alters the equation constant to 0.0958 and includes multiplying by the ratio of air's density to its molecular weight.

The results provided by Harbeck (1962), shown as Equation (2) in Table 3, were developed entirely on water evaporation measurements from reservoirs. Theoretically, since water evaporation is gas-phase controlling, these measurements can provide a measure of the gas-phase mass transfer coefficient. However, the results obtained by Mackay and Matsugu not only describe the evaporation of water, but also provide good correlation to the work of Sutton. Therefore, the selected k-value for the gas-phase (influenced by wind) is that shown by Mackay and Matsugu.

Turbulent Diffusion from Mechanical Mixing--

The literature provided limited information to describe the turbulent diffusion of a chemical within the gas-phase as a function of mechanical aeration. However, through limited experimental observations and additional investigations by Reinhardt (1977), an empirical expression has been developed to approximate the gas-phase mass transfer coefficient under aerated conditions. This relationship appears below:

$$k_G = 0.00039 \frac{\rho_g D_{i,air}}{d} (N_{Re})^{1.42} (N_{Fr})^{-0.21} (N_P)^{0.4} (N_{Sc})^{0.5}$$

(Reinhardt, 1977, as given by Hwang, 1982)

where:

k_G is in lb/ft^2-hr;

ρ_g = density of the gas (lb/ft^3);

$D_{i,air}$ = diffusion coefficient of compound i in air (ft^2/hr);

d = diameter of aerator turbine or impeller (ft);

(N_{Re}) = gas Reynolds number = $\rho_g d^2 \omega / \mu_g$;

ω = rotational speed of turbine impeller (rad/sec);

μ_g = absolute gas viscosity (g/cm-sec);

(N_{Fr}) = Froude number = $d^2 \omega / g$;

g = gravitational constant (32.17 ft/sec^2);

(N_P) = power number = $Prg/\rho_L d^5 \omega^3$;

Pr = power to the impeller (ft-lb$_f$/sec);

ρ_L = density of the liquid (lb/ft^3);

(N_{Sc}) = gas Schmidt number = $\mu_g/\rho_g D_{i,air}$;

Note: (N_{Sh}) = Sherwood number = $(k_G)d/\rho_g D_{i,air}$ and therefore;

$$(N_{Sh}) = 0.00039\ (N_{Re})^{1.42}(N_P)^{0.4}(N_{Sc})^{0.5}/(N_{Fr})^{0.21}$$

Overall Mass Transfer Coefficient (K-Value)

As described previously, correlations for determining the individual mass transfer coefficients for the soil, liquid and/or gas-phases have been developed by several researchers. However, as shown previously in Figure 2, there are seldom instances where only one phase occurs for a particular TSDF. Commonly, the mass transfer coefficients for two or more phases must be calculated to determine the overall mass transfer coefficient (K-value).

The two-phase resistance theory is used to describe transfer within multiphase systems. The theory describes the relationship between an overall mass transfer coefficient (K-value) and the individual soil, liquid and/or gas phase mass transfer coefficients (k-values) identified previously in this section. Specifically, the reciprocals of the individual mass transfer coefficients are summed and combined with the equilibrium concentration (described by the Henry's Law constant--H_i) established at either the liquid or gas interphases, thus describing the overall resistance (1/K) for the multiphase case. For example, the overall diffusion of a given contaminant from a lagoon requires the mass transfer of that contaminant through the bulk of the liquid (k_{liquid}) and through the air above the liquid (k_{gas}). In terms of the two-phase resistance theory, this multiphase phenomenon can be described as follows:

$$\frac{1}{K} = \frac{1}{k_{liquid}} + \frac{RT}{k_{gas}\ H_i}\left(\frac{C_{gas}}{C_{liquid}}\right) \qquad \text{(Hwang, 1982)}$$

where: K = overall liquid-phase mass transfer coefficient;

k_{liquid} = individual liquid-phase mass transfer coefficient;

k_{gas} = individual gas-phase mass transfer coefficient;

H_i = Henry's Law constant for compound i in atm-m^3/gmol;

RT = 0.024 atm-m^3/gmol (@ 298°K);

C_{gas}, C_{liquid} = molar densities of the gas and liquid, respectively.

However, one phase frequently dominates the overall mass transfer (or resistance, 1/K) and therefore controls the rate of mass transfer. The determining factor for this occurrence has been theoretically and experimentally found to be dependent upon the value of H_i. For example, if H_i is large (more than 10^{-3}), the liquid-phase resistance ($1/k_{liquid}$) often controls, whereas if H_i is small (less than 2×10^{-5}), the gas-phase resistance ($1/k_{gas}$) often controls.

Special Case for Overall K-Value

For the case of agitated conditions (specifically aerated impoundments), two distinct zones occur at the liquid surface: (1) turbulent, and (2) natural (convective). To describe this phenomenon using the two-phase resistance theory, it is necessary to determine the overall mass transfer coefficient for each distinct zone and sum these values, proportioned to the affected area of each zone. This can be described as follows:

$$\frac{1}{K_L^{(n)}} = \frac{1}{k_{liquid}^{(n)}} + \frac{RT}{(k_{gas}^{(n)})(H_i)} \left(\frac{C_{gas}}{C_{liquid}}\right)$$

and

$$\frac{1}{K_L^{(t)}} = \frac{1}{k_{liquid}^{(t)}} + \frac{RT}{(k_{gas}^{(t)})(H_i)} \left(\frac{C_{gas}}{C_{liquid}}\right)$$

where:

$$K_L = (K_L^{(n)}) \frac{A_n}{A} + (K_L^{(t)}) \frac{A_t}{A}$$

where: $K_L^{(n)}$ = overall liquid-phase mass transfer coefficient for the natural zone;

$K_L^{(t)}$ = overall liquid-phase mass transfer coefficient for the turbulent zone;

K_L = area-averaged overall liquid-phase mass transfer coefficient;

A_n = effective surface area of the natural zone;

A_t = effective surface area of the turbulent zone;

A = total surface area of the surface impoundment.

In order to calculate the overall mass transfer coefficient, the individual k-values for liquid and gas phases must be in similar units. Hwang (1982) has provided the following conversion method:

$$k_L \left(\frac{\text{lb-mol}}{\text{ft}^2\text{-hr}}\right) = k_L \left(\frac{\text{cm}}{\text{hr}}\right) \frac{\rho_m}{MW_m} \times \frac{(30.48)^2}{454}$$

$$k_g \left(\frac{\text{lb-mol}}{\text{ft}^2\text{-hr}}\right) = k_g \left(\frac{\text{m}}{\text{hr}}\right) \frac{\rho_{air}}{MW_{air}} \quad (3.28)$$

where: ρ_m = density of mixture (g/cm^3) (= 1 for water);

MW_m = molecular weight of mixture (= 18 for water);

ρ_{air} = density of air (lb/ft^3);

MW_{air} = molecular weight of air.

SELECTION OF MOST APPROPRIATE AERR MODELS

Once the appropriate mass transfer coefficients are selected, the model which most accurately reflects the actual emission release phenomena at TSDFs can be selected. The following paragraphs identify models selected for each TSDF-type, based on the previous discussion of k-value selection. A more detailed discussion of each model appears later in this report.

Surface Impoundment (SI) Model Selection

SI AERR models are required for four typical scenarios encountered in the field; i.e., steady-state conditions with and without mechanical aeration, and unsteady-state conditions with and without mechanical aeration. AERR models for the cases of mechanical and diffused aeration with biological activity are treated separately in Section 8. Table 4 summarizes the available models found in the literature and indicates the scenario(s) for which each model is applicable. GCA's recommended models are footnoted.

Several SI models shown in Table 4 were eliminated from consideration because they did not completely describe the theoretical conditions encountered in the field. Specifically, McCord (1981), Smith, et al (1980 and 1981), and Mackay and Wolkoff (1973), were dismissed from further consideration, as described in Table 4.

Shen (1982) modified the original Thibodeaux, Parker and Heck (1981d) nonaerated, steady-state model by incorporating; (1) the k_L relationship presented by Owens, et al (1964) which is more applicable to flowing streams (not stagnant surface impoundments), and (2) the most appropriate k_G relationship (in GCA's opinion as described earlier). Shen also suggests a simplification technique for calculating the Schmidt number based upon the compound's molecular weight. This simplification technique is described further in Section 4 of the report.

The Thibodeaux, Parker and Heck (1981d) approach appears most appropriate for estimating AERR from nonaerated SIs under steady-state conditions i.e., fairly continuous inflow of contaminants. For unsteady state nonaerated SIs, where the contaminant is discharged to the SI as a slug, or pulse injection, the Mackay and Leinonen (1975) approach appears most appropriate. Section 4 of this report elaborates on each SI model summarized herein.

TABLE 4. AERR MODELS FOR SURFACE IMPOUNDMENTS

Model	Applicability.	Primary reason for recommending or not recommending
Mackay and Wolkoff (1973)	Nonaerated Unsteady state	Not based on two-film resistance theory
Mackay and Leinonen (1975)[a]	Nonaerated Unsteady state	Only unsteady state model based on two-film resistance theory
McCord (1981)	Aerated Nonaerated Steady state	Only considers gas-phase resistance. Most chemical compounds are liquid-phase controlled
Smith, et al (1980-81)	Nonaerated Steady state	Based on two-film resistance theory, but requires complex laboratory experiments.
Thibodeaux, Parker and Heck (1981d)[a]	Aerated Nonaerated Steady state	Based on two-film resistance theory - recommended for steady-state conditions
Shen (1982)	Nonaerated Steady state	Modified Thibodeaux, Parker and Heck (1981d) model. Simplification technique for Schmidt number is provided, and k_G value used is recommended

[a] Denotes recommended models.

For aerated SIs, only two equations are available. McCord (1981) based his model on evaporation of water to address diffusion of volatile compounds. However, the evaporation of water is gas-phase controlling, whereas volatilization of most chemical compounds is liquid-phase controlling. This inaccuracy was also noted for McCord's nonaerated SI model. Only the Thibodeaux, Parker and Heck (1981d) model accurately describes the aerated SI in terms of the two-film resistance theory. Thus, Thibodeaux, Parker and Heck (1981d) is recommended for both aerated and nonaerated SIs under steady state conditions.

The Mackay and Leinonen (1975) unsteady-state model may also be applicable to an aerated impoundment. This statement is justifiable by recalling that the Thibodeaux, Parker and Heck (1981d) model is applicable to both a nonaerated and aerated SI, and is similar in form. The only difference is that the aerated impoundment must also consider liquid and gas-phase mass transfer in the turbulent zone created by mechanical aeration, in addition to the liquid and gas-phase k-values from the convective (natural) zone. These additional considerations can be incorporated into the unsteady-state model, by using the appropriate overall K-value for both the turbulent and convective zones.

Landfill Model Selection

Landfill models are required for two cases: (1) hazardous waste disposal only, and (2) codisposal of hazardous waste with solid waste material. Table 5 summarizes the available models for landfills for no gas generation, effects of biogas generation, effects of barometric fluctuations and also for open dumps. GCA's recommendations are footnoted.

Limited field validation test data makes the selection of landfill AERR model difficult at this time. The key to selecting a landfill model is an accurate description of pore diffusion as it relates to various soil matrices and moisture contents. As described in the k_{soil} subsection, the effective diffusivity for pore diffusion may be best described by a power law relationship to air-filled porosity, which appears to be dependent on soil type. Limited data for gas diffusion in wet soils complicates a similar power law relationship.

For now, GCA believes that power law relationship models deserve field validation. Field testing should include a method of determining the power law relationship of various soil mixtures and moisture contents which may be typical of hazardous waste landfill sites.

Accurately determining the effective diffusivity parameter for the AERR landfill model may only be one of many other potentially major problems to consider. Other problems include quantifying lateral gas migration, and adsorption of organic vapors onto soil. Like the effective diffusivity determination, each of these factors may also be soil specific.

Shen (1980) modified Farmers' original equation, thus introduced some simplification errors. Shen defined the air emissions of a specific component

TABLE 5. AERR MODELS FOR LANDFILLS

Model	Applicability	Primary reasons for recommending or not recommending
Farmer, et al (1978)[a]	Covered landfills	● Experimental data limited to pure component hexachlorobenzene
Shen (1980)	Covered landfills	● Simplification of Farmer's model and contains over-simplifications (see text)
Thibodeaux (1981a)[a]	Covered landfills-with no gas generation	● Defines pore diffusion in terms of soil porosity and tortuosity, but limited for dry, granular soils
Thibodeaux (1981a)[a]	Covered landfills-with biogas generation	● Describes porous media diffusion with convective effects due to biogas generation ● No experimental data
Thibodeaux, Springer, Riley (1981b)	Covered landfills-with barometric fluctuations	
Shen (1981)	Open dump	● Does not take into account vertical structure of the earth's boundary layer (Sutton) ● Limited to gas phase diffusion only

[a] Denotes recommended models.

based on its weight percent in the waste mixture. For waste mixtures, consideration of waste composition on a mole basis and the activity coefficient is important.

Thibodeaux (1981a) also provides a model for codisposal of hazardous waste with solid waste material to account for the air emissions resulting from the ascending gases. One may need to correlate the quantity of gases generated with the type and quantity of material buried and respective soil properties in order to determine the expected gas velocity. Sufficient data may exist such that a general correlation can be developed.

Thibodeaux et al. (1981b) also identify air emissions release rate for landfills which includes the effect of barometric pressure fluctuations. According to Springer (1983), computer simulation studies have shown that the effect of barometric pressure fluctuation (pumping) does not average out over long periods of time, and thus should be considered for annual AERR estimates. The effect of internal gas generation also plays an important role when hazardous waste is codisposed with solid waste. The convective effects created by the anaerobic gas generation can carry volatile vapors to the soil surface, thus increasing the flux rate.

Open Dump Models

Only one equation appeared in the literature for AERR from open dump sites, proposed by Shen (1981). Shen's equation is not considered accurate for our purposes because it neglects the vertical structure of the earth's boundary layer described by the work of Sutton (1953). The starting point for an appropriate open dump equation should be based on work conducted by Thibodeaux and Hwang (1982) for landfarming emissions. Assuming solid material in the open dump that does not intermix or seep into the soil, the flux rate can be estimated by:

$$q_i = k_{Gi} C_i X_i$$

where; k_{Gi} is the gas-phase mass transfer coefficient for component i calculated by the correlation developed by Sutton (1953) and previously described under k_G subsection; C_i equilibrium vapor concentration of compound i in g/cm^3; and X_i is the mole fraction of compound i in the waste. Sutton accurately described the gas-phase mass transfer coefficient as a function of wind speed, surface roughness, and surface length. For liquid material in an open dump, the landfarming model described below would be most appropriate.

Landfarming Model Selection

The selection of an AERR model for landfarming is relatively straightforward since only two candidates were found in the literature. The Hartley (1969) model describes AERR for landfarming operations only as a surface evaporation problem (i.e., gas phase resistance only). This may be sufficient for short-term emissions determination following initial spreading, but for landfarming, where multicomponent waste oil or sludge is generally incorporated into the soil matrix, one needs to define vapor movement in the porous soil. In addition, Hartley's evaporation model uses water evaporation as the basis (reference compound) in determining the AERR for other compounds. It does not appear correct to compare the rate of evaporation of volatile compounds to that of water.

The Thibodeaux-Hwang (1982) model correctly identifies the flux rate of a chemical compound as vapor diffusion through soil medium. The model also accounts for the soil "dry down", the increased resistance contributed by the soil phase. The effect of liquid-phase resistance is considered based on the assumption that the oil-layer diffusion length is considerably small (i.e., Z_0 less than soil particle diameter) after the oil waste is incorporated into the soil. However, one should examine the contribution of liquid-phase resistance for the initial emission release rates immediately after surface application where the oil layer thickness may be considerably larger than a soil particle size.

Although the Thibodeaux-Hwang model most accurately identifies the soil-phase resistance as a factor in air emissions for landfarming operations, it does not identify the liquid-phase resistance as probably being most important, especially for emission rate determination immediately after application where waste oil may be applied several inches thick. Typically, waste oil or sludge applied to the soil may contain many organic volatile compounds. As the liquid diffusion coefficient of a compound is generally four or five magnitudes smaller than its molecular (gas-phase) diffusion coefficient, this suggests that the liquid mass transfer coefficient should be incorporated into the short-term analysis. Assumptions made the Thibodeaux-Hwang landfarm model include:

- isothermal soil column;
- no vertical liquid movement by capillary action;
- no adsorption by soil particles; and
- no biochemical oxidation.

The use of these assumptions may not be entirely valid for landfarming operations. Thermal gradients frequently exist in the upper soil layers, thereby creating the upper movement of heat and water in soil. In addition, the purpose of landfarming is to employ the microbiological actions of the upper soil layer to degrade organic material. Thus, biochemical oxidation and gas generation will influence the air emissions rate.

Very little experimental data are available to verify this model, thus, factors such as solar radiation effects, gas generation due to biological activity, and microbiological destruction rates should be quantified when model verification tests are performed.

Storage Tank Model Selection

Models for storage tanks have long been available through EPA in the standard air emission estimation handbook, AP-42. Section 7 describes the state-of-the-art techniques recommended by EPA for fixed-roof and floating roof tanks. No models were selected for pressure tanks since emissions from such tanks are not regularly occurring events.

Air emissions from fixed roof tanks occur from breathing losses and working losses. The best available model for estimating breathing loss emissions was developed by API (1962) and modified by TRW/EPA (1981). The TRW/EPA modification was necessary since test results showed the API (1962) equation over-estimated breathing losses by approximately a factor of four. The best available model for estimating working loss emissions was developed by API in 1962. Recent test results show that this model accurately predicts emissions.

The models deemed most applicable to estimating standing storage losses and withdrawal losses from external floating roof tanks were developed by API (1980) and modified slightly by EPA (1981). Emissions estimates for internal floating roof tanks are available in API Publication 2519.

Emission factor equations in AP-42 are applicable to pure component liquids. Thus, GCA has provided a method of determining storage tank emissions for mixtures. In addition, EPA requested that GCA identify applicable AERR models for open storage tanks. Details of storage tank AERR models and these two special cases appear in Section 7.

WASTE TREATMENT PROCESSES

As suggested by OSW, the approach used for properly identifying the appropriate AERR model for the variety of treatment systems was to categorize each system into one of three main topics:

- open tank-no mixing - i.e., no disturbance of air-liquid interface;
- open tank-mixing - i.e., obvious disturbance of air-liquid interface;
- closed system - i.e., no air emissions directly from process during normal operations.

Table 6 presents each of these categories and lists typical treatment processes.

TABLE 6. WASTE TREATMENT PROCESSES

- OPEN TANK-NO MIXING
  - sedimentation
  - chlorination
  - equalization
  - anaerobic treatment
- OPEN TANK-MIXING
  - Low-rate mixing
    - neutralization
    - chemical precipitation
    - flocculation/coagulation
  - high-rate mixing
    - activated sludge process (contact stabilization)
    - aerated lagoons
    - ozonation
    - rotating biological discs
    - trickling filter
    - dissolved air flotation
- CLOSED TANK SYSTEMS - chemical separation techniques
  - steam distillation/stripping
  - extraction
  - decantation
  - ion exchange separations
  - activated carbon systems[a]
  - dialysis and electrodialysis
  - filtration

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[a] Powdered activated carbons can be used in existing tanks, filtration, or settling equipment (i.e., open tanks).

For many treatment processes, some form of reaction, chemical or biological, will occur within the tank. Assuming steady-state conditions (no fluctuations in flow or formation of additional chemical compounds) a mass balance for a specific component can determine the concentration of that component in the tank. Once the in-tank concentration of the component is known, air emissions can be estimated by applying one of the surface impoundment models previously recommended, depending upon whether or not the tank is agitated. Determining the in-tank concentration of organic compounds, however, will be related to the following:

- the compound's solubility in water;
- the compound's affinity for the formed sludge, floc, etc., versus water;
- digestion capability of microbial population within the tank.

Organic compounds removal from wastewater streams by one of the closed systems shown in Table 6, is common in the chemical and petrochemical industries. Aside from system leakage or abnormal operation, there should be no air emissions from these closed treatment systems. The effluent streams from these unit operations may go on to further treatment (biological, or cooling towers and lagoons) or disposal (surface impoundment, or landfarming), therefore it may be necessary to determine the concentrations of organics in the respective streams.

Generally, the efficiency of a processing unit (steam stripper, activated carbon bed, etc.) should be known based on laboratory or pilot scale testing. However, in the absence of efficiency data, one can calculate a systems removal efficiency based on chemical engineering principles. For instance, knowing the design of a stripping tower (i.e., tray data and flow rates) one can determine the towers efficiency. Likewise, knowing the absorptive capacity of carbon for a specific organic compound (generally through laboratory analysis) and the bed design data, the effluent concentration of wastewater can be determined.

OPEN TANK WITH MIXING

GCA's evaluation of open tank treatment processes with mixing focused mainly on the activated sludge biological treatment process (high rate mixing). Other processes which might fall into the low rate mixing subcategory would include neutralization or precipitation process involving the addition and mixing of a chemical reagent. The emissions from these processes are best described by application of Thibodeaux's ASI model using very low power input to identify the area of turbulent mixing. This model is discussed in detail in Section 4 of this report.

Biological Treatment Systems

Efforts in selecting models for predicting air emission release rates from activated sludge treatment processes focused on four models given in the literature:

- Thibodeaux (1981d)--Aerated Surface Impoundment (ASI) Model;
- Hwang (1980)--Activated Sludge Surface Aeration (ASSA) Model;
- Freeman (1979)--Activated Sludge Surface Aeration (ASSA) Model;
- Freeman (1980)--Diffused Air Activated Sludge (DAAS) Model.

All of the models presented predict the emissions release rate based on the concentration of compound i (X_i) in the aeration basin of the activated sludge (AS) process. The complexity of the models are generally dependent upon the information assumed to be unknown. The Thibodeaux (1981d) ASI model, which assumes the concentration X_i is known, is by far the simplest model. Thibodeaux applies the two-film resistance theory to predict the air stripping losses due to mass transfer at the air-water interface (aeration basin surface). Thibodeaux's model isolates zones for convective and turbulent mixing and applies appropriate mass transfer expressions for each zone. Thus, having determined an area-averaged overall mass transfer coefficient (K_L), the ASI model applies this to the concentration (X_i) in the basin to predict the air emission release rate.

Both the Hwang (1980) and Freeman (1979) ASSA model employ identical mass transfer expressions to predict emissions from the activated sludge process. These models differ from the Thibodeaux model in that they predict air emissions based on the influent concentration (S_o) of the compound (substrate). The Hwang (1980) ASSA model considers the interaction of; (1) substrate removal by biodegradation; (2) removal by air stripping; and (3) adsorption of substrate to the biomass (sludge). Whereas, the Freeman (1979) ASSA model considers biodegradation and air stripping, but ignores adsorption of substrate to the biomass. The work of Kincannon (1981,1982), discussed briefly in Section 8, also indicated that sludge adsorption was not a major pollutant removal mechanism when biodegradation, air stripping, and adsorption are considered collectively. However, other studies (Hwang, 1981; Patterson, 1981) suggest that biosorption removal may be quite significant for a number of organic priority pollutants. Both ASSA models calculate the effluent concentration (Se) based upon a steady-state equilibrium reached by the above competing removal processes. The air emission release rate is then computed by the ASI mass transfer model.

The different biooxidation rate kinetics equations selected by Hwang and Freeman lead to major differences in the complexity of each model. Hwang's ASSA model employs the relatively simple 1st order Grau kinetics to predict the rate of biooxidation. Freeman selects a biokinetic model developed by Gerber for refinery wastes, which ties the substrate removal rate to the biomass concentration, the oxygen concentration, and the substrate concentration.

Solution of Hwang's model is tedious but workable. In addition, Hwang has provided biokinetics rate data (values of $K_{1(s)}$) for a large number of organic compounds. Thus, data necessary to develop solutions based on Hwang's model are reasonably accessible. Conversely, solution of Freeman's model requires solving three simultaneous nonlinear equations for three unknowns.

Hand calculation of the solution is rather cumbersome, thus the solution is best conducted by a computerized iteration technique. In addition, biokinetic rate constants for the Gerber Model (3rd order Monod) used by Freeman have been compiled only for a limited number of compounds (acrylonitrile, benzene, styrene). Consequently, application of Freeman's ASSA model using Gerber kinetics will be limited by this data requirement. In short, the solution of the Freeman model is very complex and not well suited to EPA's intended purposes under this program.

Freeman's (1980) diffused air activated sludge (DAAS) model was the only model reviewed which adequately models diffused air systems. The DAAS model is similar to Freeman's ASSA model with the exception of the mass transfer model for air stripping. In the DAAS model, Freeman predicts the air stripping losses based on the mass transfer of the organic compound into the sparger bubbles as opposed to the surface aeration model which predicts mass transfer through the basin surface. Because the DAAS mass transfer model is slightly more sophisticated than the more empirical surface aeration (ASI) mass transfer model, Freeman's DAAS is also slightly more difficult to solve. Freeman's DAAS model assumes that the mass transfer process is liquid phase controlled and assumes that transfer occurring at the surface of the basin is negligible.

The concern in employing these models for the purpose of predicting air emission release rates is accuracy. Hwang's ASSA model is based on limited laboratory and treatment facility data. Efforts to verify the Hwang model were only moderately successful. Freeman's diffused air mass transfer model showed good agreement with verification data based on sterile process experiments. Freeman's DAAS model has been calibrated to laboratory data, however, no additional verification has been reported in the literature. Given the status of model verification presented above, concern over putting untested models into general use is warranted.

GCA recommends that the Agency employ the following models for use in air emission assessments:

- Thibodeaux (1981d) ASI model--for known effluent concentrations;
- Hwang (1980) ASSA model--for unknown effluent concentrations;
- Freeman (1980) DAAS mass transfer model--for known effluent concentrations;
- Hwang (1980) ASSA model modified after Freeman (1980) DAAS--for diffused air systems with unknown effluent concentrations.

The Hwang ASSA model is selected over Freeman's model because the Hwang model can account for adsorption to wasted sludge, employs simpler bioxidation kinetics for which rate constant data are available, and is capable of modeling adsorption of substrate to the biomass. Freeman's DAAS mass transfer equations are selected for modeling diffused air systems because they are currently the only reasonable choice. GCA recommends that the DAAS mass transfer equations be integrated into Hwang's ASSA model for predicting DAAS air emission release rates where the effluent concentration is unknown. Again, this is recommended to simplify the problem solution and to avoid costly experiments to determine Gerber's biokinetic rate constants.

WASTE PILES (PARTICULATE EMISSIONS)

EPA requested GCA to survey available information for estimating particulate emissions from waste storage piles. (Note that all other information contained in this report pertains to estimating volatile air emissions). The most approriate approach to estimating waste pile particulate emissions is the emission factor equations developed from limited field test data by the Midwest Research Institute (MRI) under contract with EPA. The MRI correlations have been frequently used by regulatory agencies in estimating particulate emissions from industrial storage piles (coal, iron ore, gravel, etc.) and are presented in Section 10 of this report. An emission factor equation in AP-42 provides a more general approach that does not account for site operational procedures.

SECTION 3

AERR MODEL VALIDATION EFFORTS REPORTED IN THE LITERATURE

INTRODUCTION

The AERR models have generally not been validated or calibrated by comparison with a substantial field data base. Only three test reports or reference articles reported comparisons between predictive AERR models and actual field measurements at the end of 1982. Additional reports provided ambient air monitoring data which cannot be directly applied to the AERR models without back-calculating the AERR via a dispersion model. However, some field work aimed at model validation is currently underway (IERL-Cincinnati with Thibodeaux, et al.) and in the planning stages for 1983 (IERL-Cincinnati with Radian Corporation and OSW - Engineering Science, Inc.).

This section summarizes model validation efforts conducted prior to 1983.

AERR MODEL COMPARISON WITH FIELD DATA

Table 7 lists four reports in which measured AERR were compared with predictive modeling equations. Test data from the most recent sampling of surface impoundment air emissions by Thibodeaux, et al. (1982) appear most promising. Initial comparisons indicate that the predictive model estimates are within a factor of two to three of the measured emission rate.

Thibodeaux, Parker and Heck (1981d)

The objectives of this report were to develop a measurement technique for volatile organic carbon (VOC) emissions emitted from wastewater treatment basins and to develop a mathematical model that would predict emission rates. The concentration-profile (CP) technique was used for determining the flux rate of methanol, acetone and total hydrocarbon emissions. The following individual mass transfer correlations were used in the predictive model:

- k_g (convective)--Harbeck;
- k_g (turbulent)--Reinhardt;
- k_l (convective)--Cohen;
- k_l (turbulent)--Thibodeaux, Parker.

TABLE 7. AERR MODEL VALIDATION EFFORTS

Test report	Authors (date)	Comparisons made
Measurement of Volatile Chemical Emissions from Wastewater Basins	Thibodeaux, Parker, Heck (1981d)	Development of concentration-profile technique: comparisons of measured methanol flux rates with predictive model
Evaluation of VOC Emissions from Wastewater Systems (Secondary Emissions) Draft Report	Cox, Steinmetz, Lewis (1982)	Concentration-profile technique measurements compared to predictive model for aerated and nonaerated conditions
Air Emission Monitoring of Hazardous Waste Sites	Thibodeaux, Springer, Lunney, James, Shen (1982)	Concentration-profile technique measurements compared to predictive model for aerated and nonaerated conditions
Suggested Control Measures to Reduce Organic Compound Emissions Associated with Volatile Organic Waste Disposal	Ames, Shiroma, Wang, Lam, O'Brien (1982)	Comparisons of measured land-treatment emission rates with Hartley and Thibodeaux-Hwang models

Although flux rate measurements were made for methanol, acetone and total hydrocarbon, only methanol data were used in the predictive model comparison effort. The authors decided not to use acetone in the comparison because of uncertain water chemistries at the low concentrations encountered. Chemistry data with correlation coefficients of less than 0.8 were excluded. The following flux rate comparisons were reported:

- measured--1.4 to 3.8 ng/cm^2-sec (11 to 29 lb/acre-day);
- predicted--0.37 to 5.9 ng/cm^2-sec (2.8 to 45 lb/acre-day).

The comparison of all four mass transfer coefficients indicated that methanol volatilization is gas-phase controlling.

Cox, Steinmetz and Lewis (1982) - Draft Report

This draft report compares the measured air emissions from two wastewater treatment facilities to results obtained by using the predictive model. The CP technique was used to measure chemical flux rates from an aerated and a nonaerated pond. The following individual mass transfer correlations were used in the predictive model:

- k_g (convective)--Mackay, Matsugu;
- k_g (turbulent)--Reinhardt;
- k_l (convective)--Cohen;
- k_l (turbulent)--Thibodeaux.

A Final Report was not available for review, but the following preliminary results were noted. Predictive flux rates initially reported ranged from 15 to 38 percent of measured flux rates for nonaerated conditions, and from 0.1 to 2.5 percent of measured flux rates for the aerated site. However, in applying the predictive model equation, the approach used for calculating the equilibrium constant was incorrect. The use of Raoult's law may be only applicable to hydrocarbon mixtures, not to aqueous solutions. Henry's law, or the use of an activity coefficient are more correct approaches. Field data from this report may still be valuable subsequent to complete peer review and verification of results.

Thibodeaux, et al. (1982)

The work presented in this paper identified the emission rates of two surface impoundments (one aerated and one non-aerated) at a hazardous waste facility. Measurements at the site by the CP techniques provided data to "field test" the emission release rate models for chemicals in which the mass transport process is liquid-phase controlled. Additionally, the authors identified the capability of the CP technique in detecting and quantifying absorption and vaporization from area source. Comparison of calculated flux rate versus measured flux rate for 1,1-dichloroethane and benzene were found to be within a factor of ±2.

Ames, et al. (1982)

In an attempt to illustrate the difference between the Hartley and Thibodeaux-Hwang AERR models for landfarming, this report provided sample calculations based on experimental data. Figure 6 shows the predictive results of the two models and also displays the experimental results. The experimental data were not available to GCA, thus the variables and assumptions used in the calculations could not be verified.

One limitation of the Hartley model, clearly illustrated in Figure 6, is the assumption of a maximum emission rate throughout the exposure period. The Thibodeaux-Hwang model only slightly underpredicts the measured results.

ADDITIONAL DATA AVAILABLE

Additional test reports contain ambient air emissions monitoring data for hazardous waste facilities. A document prepared by Fred C. Hart Associates, entitled "Development of a Data Base on Air Emissions from Hazardous Waste Facilities," provided a cursory review of 21 hazardous waste site reports received from the 10 EPA regions. It is not known if data provided in the original test reports are adequate for application to the various AERR models. This data base may need further review.

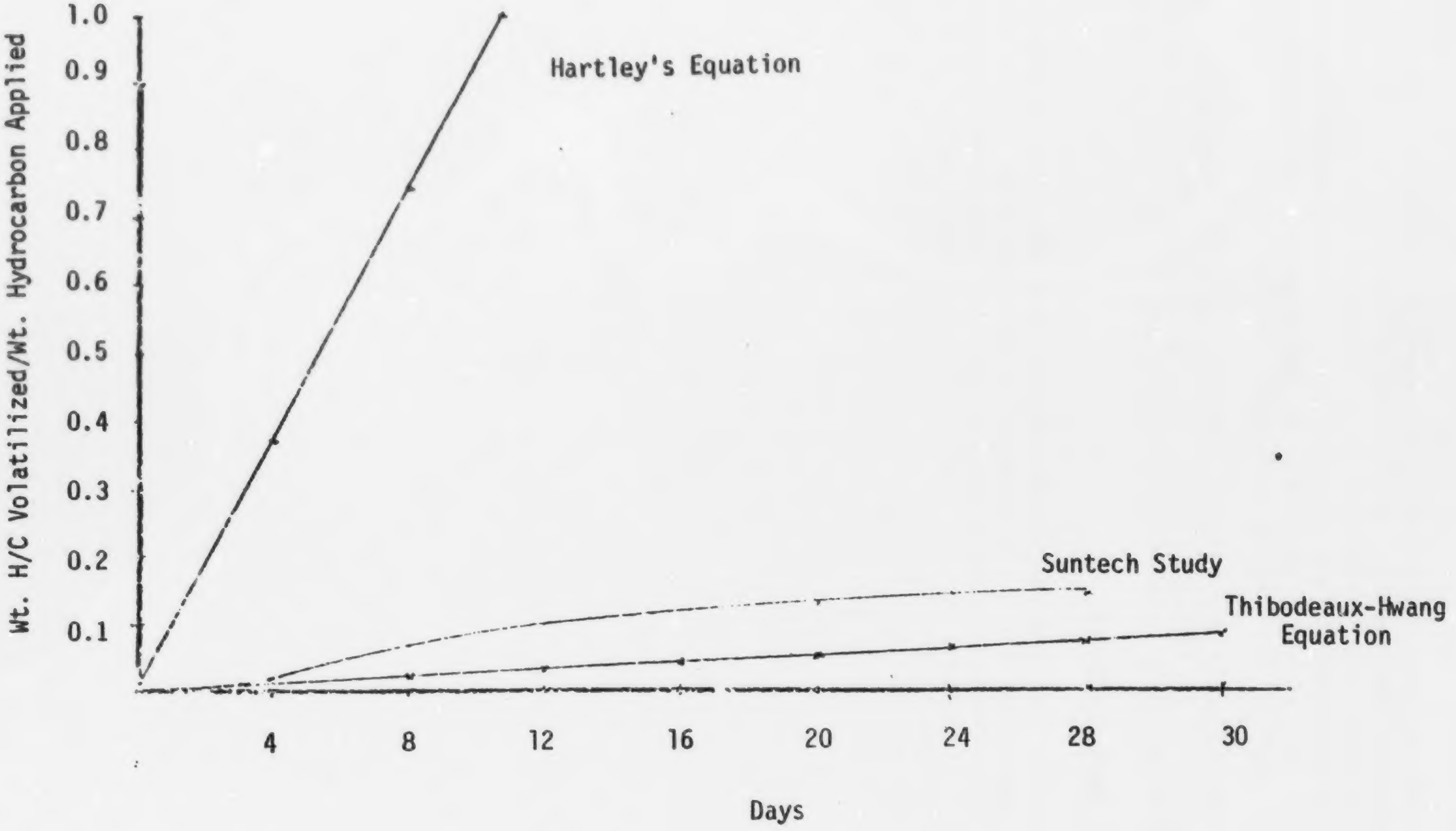

Figure 6. Comparison of Hartley and Thibodeaux-Hwang landfarming AERR models with measured air emissions data (Ames, et al., 1982).

SECTION 4

REVIEW OF SURFACE IMPOUNDMENT AERR MODELS

INTRODUCTION

Surface impoundments (SIs) are defined in Chapter 40, CFR Part 260, Subpart B, Section 260.10 (amended by 46 FR 27476, May 20, 1981) as "a facility or part of a facility which is a natural topographic depression, man-made excavation, or diked area formed primarily of earthen materials (although it may be lined with man-made materials) which is designed to hold an accumulation of liquid wastes or wastes containing free liquids, and which is not an injection well. Examples of surface impoundments are holding, storage, settling, and aeration pits, ponds, and lagoons."

This section presents all models for SIs found in the literature. GCA's recommendations for SI models and mass transfer coefficients were presented previously in Section 2.

Eight models or variations thereof appear in the literature for estimating the air emission release rates (AERR) from SIs (nonaerated and aerated) as follows:

- Mackay and Wolkoff (1973) unsteady-state, nonaerated;
- Mackay and Leinonen (1975) unsteady-state, two-film theory, nonaerated model;
- Thibodeaux, Parker and Heck (1981d) steady-state, two-film theory one nonaerated and one aerated model;
- Shen (1982) modification of Thibodeaux, Parker and Heck nonaerated model;
- Smith, et al. (1980-81) steady-state, first-order kinetic, nonaerated model;
- McCord (1981) steady-state, modified Nusselt equation, one nonaerated and one aerated model.

In addition, the literature contains a calculational model, proposed by Thibodeaux, Parker, Heck and Dickerson (1981c). This model is not suitable for our purposes since detailed field measurements are required as input data.

The eight predictive models can be categorized according to their theoretical basis. Five of the eight models incorporate the two-film resistance theory. The three predictive models that are not based on the two-film resistance theory have been criticized by more recent research. For example, the two predictive models presented by McCord (1981) are based on the Nusselt equation, not the two-film resistance theory. The theoretical basis of water evaporation implied by the Nusselt equation is considered a unrealistic approach to the volatilization process of most sparingly (slightly) soluble organics. The Mackay and Wolkoff (1973) predictive model is not based on the two-film resistance theory and was essentially revised by Mackay and Leinonen's 1975 research.

Models which incorporate the two-film resistance theory are considered the most accurate methods of describing the actual volatilization process, and subsequent flux rate of an individual compound into the atmosphere. However, the models based on this theory require determining the individual liquid (k_L) and gas-phase (k_G) mass transfer coefficients for each compound of interest. The availability of liquid and gas-phase k-values is limited, and are primarily based on laboratory experiments or on field measurements of lakes, rivers, and the ocean. Consequently, the accuracy of all available state-of-the-art models is somewhat in question due to problems involved with precisely determining k-values for specific situations at TSDFs.

Table 8 summarizes input parameters required for each model reviewed by GCA. Following sections describe all models available for aerated and nonaerated surface impoundments.

NONAERATED SURFACE IMPOUNDMENTS

AERR models found in the technical literature for nonaerated SIs are reviewed below. The summary in Section 2 previously presented GCA's selections for each SI type.

Mackay and Wolkoff (1973)

Mackay and Wolkoff (1973) proposed a model to quantify the volatilization of low solubility compounds (hydrocarbons and chlorinated hydrocarbons) from rivers, lakes and oceans. Their approach was based on equilibrium thermodynamic principles of water evaporation, in contrast with more recent research which is based on mass transfer principles of a concentration gradient across an interface. Mackay and Wolkoff assumed that the AERR could be calculated on the basis of water evaporation and the ratio of the contaminant to water in the vapor. This approach assumes that the diffusion or mixing in the water phase is sufficiently fast so the concentration of the contaminant at the water-air interface is close to that in the bulk of the water body. However, recent research on mass transfer rates suggests that diffusion in the water phase is the rate controlling variable for most low-solubility compounds. In other words, current mass transfer theory shows that the basic assumption in the Mackay and Wolkoff model is inappropriate for modeling AERR from hazardous waste SIs. Other stated assumptions in the Mackay and Wolkoff model include:

TABLE 8. INPUT PARAMETERS REQUIRED FOR EACH SURFACE IMPOUNDMENT MODEL

Parameter	Mackay (1975)[a]	Thibodeaux (1981d)[b]	Shen (1982)[c]	Smith (1980-81)[d]	McCord (1981)[e]
N, mass flux rate of compound i across the phase boundary	X				
$K_{i,L}$ overall liquid phase mass transfer coefficient of compound i	X	X	X		
$k_{i,L}$ individual liquid phase mass transfer coefficient of compound i	X	X	X	X	
$k_{i,G}$ individual gas phase mass transfer coefficient	X	X	X	X	
R, ideal gas law constant	X			X	
T, temperature	X		X	X	
H_i, Henry's Law Constant	X		X	X	
C_i, concentration of compound i at time t	X		X		
C_{io}, concentration of compound i at zero time	X				
L, impoundment depth	X		X	X	
P_i, equilibrium partial pressure of compound i in the vapor	X				X
P_{is}, vapor pressure of compound i	X				
C_{is}, solubility of compound i in water	X				
Q_i, rate of air emissions of compound i		X	X		
K, constant establishing equilibrium between the liquid and air phases		X	X		
x_i, mole fraction of compound i in the liquid phase		X			
A, surface area of the disposal facility		X	X		
MW_i, molecular weight of compound i		X	X		

(continued)

TABLE 8 (continued)

Parameter	Mackay (1975)[a]	Thibodeaux (1981d)[b]	Shen (1982)[c]	Smith (1980-81)[d]	McCord (1981)[e]
Re*, roughness Reynolds number		X			
$MW_{benzene}$, molecular weight of benzene		X			
U_{air}, wind speed		X	X		X
N_{Sc}, gas Schmidt number		X	X		
μ_g, absolute gas viscosity		X			
ρ_g, density of gas		X			
$D_{i,air}$, diffusion coefficient of compound i in air		X			
ρ_{air}, density of air		X			
MW_{air}, molecular weight of air		X			
$ERP_i = Q_i$					
$K_{oa} = K_{iL}$, overall liquid phase mass transfer coefficient					
H = L, depth of lagoon					
P, total pressure			X		
M, average molecular weight of liquid			X		
Z, length of lagoon surface				X	X
R_v, volatilization rate				X	
$k_v c$, volatilization rate of compound c				X	
E_s, evaporation rate at steady state					X
E_o, initial evaporation rate					X
L_s, amount of compound in lagoon at steady state					X

(continued)

TABLE 8 (continued)

Parameter	Mackay (1975)[a]	Thibodeaux (1981d)[b]	Shen (1982)[c]	Smith (1980-81)[d]	McCord (1981)[e]
L_o, initial amount of compound in lagoon					X
%, weight of percent of compound in water or lagoon liquid					X
VP = P_{is}, vapor pressure of the compound					
u_o = U_{air}, wind speed					
K, amount of compound in feed stream					X
F, feed rate to lagoon					X
V, operating volume of lagoon					X
sp. gr., specific gravity of liquid waste					X
N_B = N_i, flux rate					
D_{Bl} = $D_{i,air}$, diffusivity of compound i in air					

(continued)

NOTES FOR TABLE 8:

MODEL DEFINITIONS--AS PRESENTED IN THE LITERATURE

[a] Mackay and Leinonen - Unsteady-State Predictive Model for Nonaerated Surface Impoundments.

(1) $N_i = K_{iL} \quad (C_i - P_i/H_i)$

(2) $\frac{1}{K_{iL}} = \frac{1}{k_{iL}} + \frac{RT}{H_i \, k_{iG}}$

(3) $C_i = C_{io} \exp \left(-K_{iL} \, t/L\right)$

(4) $P_i = C_i \, P_{is}/C_{is}$

[b] Thibodeaux, Parker and Heck-Steady-State Predictive Model for Nonaerated and Aerated Surface Impoundments.

(1) $Q_i = K_L A \, (x_i - x_i{*}) \, MW_i$

(2) $\frac{1}{K_L} = \frac{1}{k_L} + \frac{1}{K \, k_G}$

[c] Shen's Simplification of the Steady-State Predictive Model Proposed by Thibodeaux, Parker and Heck.

(1) $(ERP)_i = (18 \times 10^6) \, K_{oA} \, AC_i$

(2) $\frac{1}{K_{oA}} = \frac{1}{k_L} + \frac{1}{K \, k_G}$

(3) $k_L = (4.45 \times 10^{-3}) \, M_i^{-0.5} \, (1.024)^{t-20} \, U_o^{0.67} H^{-0.85}$

(4) $K = (H_i/PM) \times 10^6$

(5) $k_G = (8.05 \times 10^{-4}) \, M_i^{-1} \, U_o^{0.78} \, Z^{-0.11} \, Sc^{-0.67}$

[d] Smith, Bomberger and Haynes - First Order Kinetic Equation for Nonaerated Surface Impoundments.

(1) $R_v = \frac{-d(c)}{dt} = k_v^{\,c} \, (c)$

NOTES FOR TABLE 8 (continued):

(2) $$k_v{}^c = \frac{1}{L} \left[\frac{1}{k_L{}^c} + \frac{RT}{H_c \; k_G{}^c} \right]^{-1}$$

[e] McCord's Steady-State Predictive Model for Nonaerated Surface Impoundments.

(1) $$E_s = \frac{E_o \; L_s}{L_o}$$

(2) $$E_o = 0.53425 \; A_m \; {\frac{D}{L}}^{0.22} \; (\%) \; (V_p) \; (W_o)^{0.78}$$

(3) $$L_s = \frac{K}{1-X}$$

(4) $$1-X = \frac{E_o}{L_o} + \frac{F}{V}$$

(5) $$K = 0.0834 \; (F) \; (\%) \; (\text{sp. gr.})$$

(6) $$L_o = 0.0834 \; (V) \; (\%) \; (\text{sp. gr.})$$

[f] McCord's Steady-State Predictive Model for Aerated Surface Impoundments

(1) $$E_s = \frac{E_o \; L_s}{L_o}$$

(2) $$E_o = \frac{150.315}{(460+T)} \; \frac{H}{r} \; \frac{L_o}{V_L} \; \frac{\text{V.P.}}{\text{sp.gr.}} \; \frac{d}{\pi} \; \frac{1}{\sqrt{0.17678R^{1/2}}}$$

(3) $$L_s = \frac{k}{1-x}$$

(4) $$1-x = \frac{E_o}{L_o} + \frac{F}{V}$$

(5) $$K = 0.0834(F)(\%)(\text{sp.gr.})$$

(6) $$L_o = 0.0834(V)(\%)(\text{sp.gr.})$$

- The contaminant is truly in solution, not in suspended, collodial, ionic, complexed, or absorbed form.
- The vapor formed is in equilibrium with the liquid at the interface.
- The water evaporation rate is negligibly affected by the presence of the contaminant.

Dilling's (1977) preliminary work indicated that the Mackay and Wolkoff model was inadequate since neither absolute nor relative predicted rates were in agreement with experimental data.

Mackay and Leinonen (1975)

Mackay and Leinonen (1975) extended Mackay's 1973 research in order to develop a more realistic AERR estimate for low-solubility compounds from the entire water body, and not just from the water surface. Mackay and Leinonen incorporated the work of Liss and Slater (1974) to develop an unsteady-state model to determine the AERR of a single compound. Liss and Slater applied the two-film resistance theory to estimate the flux of gases across the air-ocean interface. Contrary to Mackay's 1973 thermodynamic model theory, Liss and Slater's 1974 work suggested that for most low-solubility gases, the water (liquid) phase controls; i.e., the liquid phase offers more resistance to contaminant transport than through the gas phase.

The details of the Mackay and Leinonen model appear in Table 9. The model is based on unsteady state conditions; i.e., the chemical contaminant of interest enters the water body in a discrete slug as a pulse injection. All other SI models are based on steady state conditions; i.e., a fairly constant influx of the contaminant into the SI. As in the case of all other predictive models for nonaerated SIs, this model simplifies the actual situation by assuming well-mixed air and water phases separated by an interface with near stagnant films of air and water on either side. Thermoclines; i.e., other rate-limiting diffusion processes at depths in the water body, are not considered in this model. The Mackay and Leinonen model can be simplified by assuming that... "if P_i is negligible; i.e., the background atmospheric level of the contaminant is low compared to the local level..." then the unsteady-state flux equation becomes:

$$N_i = K_{iL}C_i$$

where: $C_i = C_{io}\exp(-K_{iL}t/L)$

$$\frac{1}{K_{iL}} = \frac{1}{k_{iL}} + \frac{RT}{(H_i k_{iG})}$$

In 1975, the only technique apparently available to Mackay and Leinonen for calculating the mass transfer coefficients (k-values for gas and liquid phases) was the 1974 Liss and Slater work shown below:

$$k_{iL} = k_{L,CO_2} \left(\frac{MW_{CO_2}}{MW_i}\right)^{0.5}$$

TABLE 9. MACKAY AND LEINONEN UNSTEADY-STATE PREDICTIVE MODEL FOR NON AERATED SURFACE IMPOUNDMENTS

Model Form:

$$N_i = K_{iL} (C_i - P_i/H_i)$$

where;

$$\frac{1}{K_{iL}} = \frac{1}{k_{iL}} + \frac{RT}{H_i k_{iG}}$$

$$C_i = C_{io} \exp (-K_{iL} t/L)$$

$$P_i = C_i P_{is}/C_{is}$$

Definition of Terms:

N_i = mass flux rate of compound i across the phase boundary (mol/m^2-hr)

K_{i_L} = overall liquid phase mass transfer coefficient of compound i (m/hr)

k_{iL} = individual liquid phase mass transfer coefficient of compound i (m/hr)

k_{iG} = individual gas phase mass transfer coefficient of compound i (m/hr)

R = ideal gas law constant (8.2 x 10^{-5} atm-m^3/mol°K)

T = temperature (°K)

H_i = Henry's law constant of compound i (atm-m^3/mol)

C_i = concentration in mol/m^3 of compound i at time t (hr)

C_{io} = concentration in mol/m^3 of compound i at zero time

L = impoundment depth (m)

P_i = equilibrium partial pressure of compound i in the vapor (atm)

P_{is} = vapor pressure of compound i (atm)

C_{is} = solubility of compound i in water (mol/m^3)

and

$$k_{iG} = k_{G,H_2O} \left(\frac{MW_{H_2O}}{MW_i}\right)^{0.5}$$

where:

k_{L,CO_2} = liquid phase mass transfer coefficient of CO_2 = 20 cm/hr (reported to be at the sea surface);

MW_{CO_2} = molecular weight of CO_2 (44 g/g mole);

MW_i = molecular weight of compound i;

k_{G,H_2O} = gas phase mass transfer coefficient of H_2O = 3,000 cm/hr (reported to be at the sea surface);

MW_{H_2O} = molecular weight of H_2O (18 g/g mole).

As described in the following sections, one emphasis of more recent research has been refinement of techniques for calculating the individual liquid and gas phase k-values.

Thibodeaux, Parker and Heck (1981d) Including Hwang (1982) and Shen (1982) Modifications

Thibodeaux, Parker and Heck proposed a steady-state model that assumes a constant influx of contaminant, as opposed to Mackay and Leinonen's unsteady state model. The Thibodeaux, Parker and Heck model, shown in Table 10, is also based on the two-film resistance theory. Empirical relationships for mass transfer coefficients developed from laboratory and field experiments at lakes, rivers and oceans were incorporated (Cohen, Cocchio and Mackay-1978; Mackay and Matsugu-1973; Owens, Edwards and Gibbs-1964). Although the k-values incorporated by Thibodeaux, Parker and Heck represent an improved data base compared to Mackay and Leinonen's approach, the calculation became substantially more complex as shown in Table 11. Some of the input parameters for these k-values are difficult to obtain, calculate or estimate, and in some cases, require field or laboratory measurement.

Hwang (1982) presented a simplified technique for determining the mass transfer coefficients for various compounds by referring to a typical compound whose k-values are known. In his review of several laboratory experiments, Hwang suggests that the k-values for oxygen and water vapor can be used to determine the k-value for the compound of interest. In his examples, the k-values for the reference compounds are based on a temperature of 25°C. The approach for calculating mass transfer coefficients identified in Hwang's paper appear in Table 12.

To apply Hwang's simplified equations, the liquid phase mass transfer coefficient for oxygen and the gas phase mass transfer coefficient for water vapor must be determined either from: (1) published data; or (2) calculating from the empirical relationships shown previously in Table 11 (the latter

TABLE 10. THIBODEAUX, PARKER AND HECK STEADY-STATE PREDICTIVE MODEL FOR NON AERATED SURFACE IMPOUNDMENT

Model Form:

$$Q_i = K_L A\,(x_i - x_i^*)\,MW_i$$

where;

$$\frac{1}{K_L} = \frac{1}{k_L} + \frac{1}{Kk_G}$$

and;

$x_i^* = 0$ since y_i is negligible in comparison to x_i

therefore,

$$Q_i = K_L A\,(x_i)\,MW_i$$

Definition of Terms:

Q_i = rate of air emissions of compound i (g/sec)

K_L = overall liquid phase mass transfer coefficient of compound i (g-mol/cm^2-sec)

k_L = individual liquid phase mass transfer coefficient of compound i (g-mol/cm^2-sec)

k_G = individual gas phase mass transfer coefficient of compound i (g-mol/cm^2-sec)

K = constant establishing equilibrium between the liquid and air phases, expressed by $y_i = Kx_i$ (Henry's law constant in mole fraction form).

x_i = mole fraction of compound i in the liquid phase = $C_{iL}\,(MW_w/MW_i)$

A = surface area of the disposal facility (cm^2)

MW_i = molecular weight of compound i (g/g-mol)

MW_w = molecular weight of water (18 g/g-mol)

TABLE 11. SUMMARY OF EMPIRICAL RELATIONSHIPS TO DETERMINE THE INDIVIDUAL LIQUID AND GAS PHASE MASS TRANSFER COEFFICIENTS FOR A NONAERATED IMPOUNDMENT

Liquid Phase Coefficient (k_L):

[1] $k_L = \left(11.4\ Re^{*0.195} - 5\right)\left(\frac{MW_{benzene}}{MW_i}\right)^{0.5}$ (Cohen, Cocchio and Mackay, 1978)

for $0.11 < Re^* \leq 102$, where k_L is in cm/hr and

$$Re^* = \frac{7.07 \times 10^{-3}\ (Z_{10})\ (U_{10})^{1.25}}{Va\ \exp\ (56.6/U_{10}{}^{0.25})}$$

if $Re^* < 0.11$, then $k_L = 2.4$ cm/hr

where;

Re^* = roughness Reynolds number

$MW_{benzene}$ = molecular weight of benzene (78.1 g/g-mole)

MW_i = molecular weight of compound i (g/g-mole)

U_{10} = wind velocity (cm/s) measured at height Z_{10} (10 m) above the water surface (cm)

Va = air kinematic viscosity (cm^2/sec)

[2] $k_L = (1.3\ Re^{*0.195} - 0.57)\left(\frac{D_{i,\ H_2O}}{D_{TOL,H_2O}}\right)$ (Cohen, et al. as presented by Hwang, 1982)

where;

k_L is in lb-mol/ft^2-hr. (Note: This equation is a modified form of equation 1 to obtain the k_L value in units of lb-mol/ft^2-hr).

Re^* = roughness Reynolds number (determined as above)

D_{i,H_2O} = diffusion coefficient of compound i in water (cm^2/sec)

D_{TOL,H_2O} = diffusion coefficient of toluene in water (cm^2/sec)

(continued)

TABLE 11 (continued)

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[3] $k_L = 3.12\,(1.024)^{\theta-20}\,U_o^{0.67}\,H_o^{-0.85}\left(\frac{D_{i,H_2O}}{D_{O_2,H_2O}}\right)$ (Owens, Edwards and Gibbs, 1964, as presented by Hwang, 1982)

where;

k_L is in lb-mol/ft^2-hr

θ = temperature (°C)

U_o = surface velocity, ft/sec, normally 0.035 x wind speed (ft/sec) for natural surface, and 0.1 ft/sec for outside region of effect of aerators in the biological treatment.

H_o = effective depth of surface impoundment (ft)

D_{O_2,H_2O} = diffusion coefficient of oxygen in water (cm^2/sec)

Gas Phase Coefficient (k_G):

[1]

$k_G = 0.0958\,U_{air}^{0.78}\,N_{sc}^{-0.67}\,d_e^{-0.11}\,\frac{\rho_{air}}{MW_{air}}$ (MacKay and Matsugu, 1973)

where;

k_G is in lb-mol/ft^2-hr

U_{air} = wind speed (m/hr)

N_{Sc} = gas Schmidt number = $\mu_g/\rho_g D_{i,air}$

μ_g = absolute gas viscosity (g/cm-sec)

ρ_g = density of gas (g/cm^3)

$D_{i,air}$ = diffusion coefficient of compound i in air (cm^2/sec)

d_e = effective diameter of the quiescent area of the impoundment (m) = $\left(\frac{4Ac}{\pi}\right)^{0.5}$

A_c = area of convective (natural) zone of impoundment surface (m^2)

ρ_{air} = density of air (lb/ft^3)

MW_{air} = molecular weight of air (28.8 lb/lb-mole)

(continued)

TABLE 11 (continued)

[2] $k_G = 0.03 \left(\frac{D_{AA}}{D_{WA}}\right) V_8/A^{0.05}$ (Thibodeaux and Parker, 1974)

where;

k_G is in lb-mol/ft^2-hr

D_{WA} = diffusivity of water vapor in air (cm^2/sec)

D_{AA} = diffusivity of compound A in air (cm^2/sec)

V_8 = wind speed at 8 meters above the water surface (miles/hr)

A = surface area of water body (acres)

TABLE 12. HWANG's (1982) SIMPLIFICATION OF THE EMPIRICAL LIQUID AND GAS PHASE MASS TRANSFER COEFFICIENTS FOR A NONAERATED IMPOUNDMENT

Liquid Phase Coefficient of Compound i ($k_{L,i}$):

$$k_{L,i} = \left(\frac{MW_{O_2}}{MW_i}\right)^{0.5} \left(\frac{273 + \theta}{298}\right) k_{L,O_2}$$

Gas Phase Coefficient of Compound i ($k_{G,i}$):

$$k_{G,i} = \left(\frac{MW_{H_2O}}{MW_i}\right)^{0.335} \left(\frac{273 + \theta}{298}\right)^{1.005} k_{G,H_2O}$$

where;

MW_{O_2} = molecular weight of oxygen (g/g-mole)

MW_{H_2O} = molecular weight of water vapor (g/g-mole)

MW_i = molecular weight of compound i (g/g-mole)

θ = temperature of concern (°C)

k_{L,O_2} = liquid-phase mass transfer coefficient of oxygen at 25°C (g-mol/cm^2-sec)

k_{G,H_2O} = gas phase mass transfer coefficient of water vapor at 25°C (g-mol/cm^2-sec)

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case is more accurate). Therefore, from these deterministic equations, the complex empirical relationships remain a key variable in obtaining either the liquid and/or gas phase mass transfer coefficients for the compound of interest.

Shen (1982), using the rate expression proposed by Thibodeaux et al. (1981d), described a simplifying method for estimating the volatilization rate of volatile organic compounds from waste lagoons. Shen's modifications included the use of Owen's correlation for k_L determination and the use of Mackay and Matsugu's correlation for k_G. Owen's correlation was obtained from reaeration studies of flowing streams, and thus may not be directly applicable to stagnant waste lagoons. For both k_L and k_G, Shen made some calculation errors in converting the units of the original correlations. Thus, correlations shown previously in Table 8 should be modified as shown in Table 11.

In applying MacKay and Matsugu's correlation, Shen suggests a molecular weight dependency for Schmidt number determinations, such that the following simplification could be employed:

Molecular Weight	$Sc^{-0.67}$
Less than 100	0.7
100-200	0.6
More than 200	0.5

Smith, Bomberger and Haynes (1980-1981)

Smith, Bomberger and Haynes proposed a technique for determining an overall volatilization rate constant based on laboratory measurements. The volatilization rate constant is essentially the overall K-value that represents the individual liquid and gas phase k-values combined. If found adequate, this approach would eliminate the complex empirical relationships for determining the individual values proposed by other researchers.

Smith, Bomberger and Haynes essentially expanded on several concepts presented by Liss and Slater (1974); i.e., (1) mass transfer in the liquid phase controls more than 95 percent of the volatilization rate if H_c (Henry's law constant) is greater than approximately 3500 torr-LM^{-1} (0.0044 atm-m^3-mol^{-1}); (2) if H_c is less than approximately 10 torr-LM^{-1} (1.2×10^{-5} atm-m^3-mol^{-1}), mass transfer in the gas phase controls more than 95 percent of the volatilization rate; and (3) if H_c is between 10 and 3500 torr-LM^{-1}, both gas and liquid phase mass transfer are important. Smith, Bomberger and Haynes categorized chemicals from these three classifications as high, low, and intermediate volatility compounds, respectively. A technique was developed for estimating the volatilization rate constant ($k_v{}^c$) for each class of volatile compounds. Table 13 shows these three estimation techniques and the model equation presented by Smith, et al. appears in Table 14.

TABLE 13. SUMMARY OF TECHNIQUES DEVELOPED BY SMITH, BOMBERGER AND HAYNES TO ESTIMATE THE VOLATILIZATION RATE CONSTANT (k_v^c) FOR HIGH, LOW AND INTERMEDIATE VOLATILITY COMPOUNDS

High-Volatility Compounds (H_c > 3,500 torr-LM^{-1}):

$$k_v^c = \left(k_v^c/k_v^o\right)_{lab} \times \left(k_v^o\right)_{env}$$

where;

k_v^c = volatilization rate constant of compound c (hr^{-1})

$\left(k_v^c/k_v^o\right)_{lab}$ = ratio of volatilization rate constants for compound c and oxygen measured simultaneously in the laboratory (shown to be a constant for high-volatility compounds

$\left(k_v^o\right)_{env}$ = oxygen reaeration constant in a real water body $\left(k_v^o\right)_{env}/L$, since the second term in the two-film resistance theory model is small compared to the first for high-volatility compounds

Low-Volatility Compounds (H_c < 10 torr-L M^{-1}):

$$k_v^c = \left(k_v^c/k_v^w\right)_{lab} \times \left(k_v^w\right)_{env}$$

where;

k_v^c = volatilization rate constant of compound c (hr^{-1})

$\left(k_v^c/k_v^w\right)_{lab}$ = ratio of volatilization rate constants for compound c and water vapor measured simultaneously in the laboratory (shown to be a constant for low-volatility compounds)

$\left(k_v^w\right)_{env}$ = $k_g^w H_c/LRT$, since the first term in the two-film resistance theory is small compared to the second for low-volatility compounds

k_g^w = gas phase mass transfer coefficient for water, determined from Fick's law, i.e., $N^w = k_g^w\ (P_s^w - P^w)/RT$

where;

(continued)

TABLE 13 (continued)

N^W = measured water evaporation flux rate (mol/cm^2-hr)

P_s^W = saturated partial pressure of water at temperature T

P^W = actual partial pressure of water at temperature T

Intermediate Volatility Compounds (H_c = 10 to 3500 torr-LM^{-1}):

Combines the estimation techniques of both high- and low-volatility compounds.

TABLE 14. SMITH, BOMBERGER AND HAYNES FIRST ORDER KINETIC EQUATION FOR NONAERATED SURFACE IMPOUNDMENTS

Model Form:

$$R_v = \frac{-d(c)}{dt} = k_v{}^c\ (c)$$

$$k_v{}^c = \frac{1}{L}\left[\frac{1}{k_L{}^c} + \frac{RT}{H_c k_G{}^c}\right]^{-1}$$

Definition of Terms:

R_v or $\frac{-d(c)}{dt}$ = volatilization rate of compound c from water (mg/l-hr)

$k_v{}^c$ = volatilization rate constant of compound c (hr^{-1})

L = length of impoundment (cm)

$k_L{}^c$ = individual liquid phase mass transfer coefficient of compound c (cm/hr)

$k_G{}^c$ = individual gas phase mass transfer coefficient of compound c (cm/hr)

R = ideal gas constant (L torr/°K mol)

T = temperature (°K)

H_c = Henry's law constant (torr L/mol)

The key limitation to the Smith, Bomberger and Haynes approach is that laboratory determinations of the ratios $(k_v{}^c/k_v{}^o)$ and $(k_v{}^c/k_v{}^w)$ are compound specific, sophisticated and expensive. Only a very limited number of compounds have been tested to date. Using other methods for determining these ratios; i.e., using values of the diffusion coefficients, increase the overall uncertainty of this model.

McCord (1981)

A fourth predictive model for estimating the emission rate of volatile compounds from nonaerated lagoons was presented by McCord (1981). This steady-state model, shown in Table 15, was based upon Nusselt's equation which describes water evaporation rates from a lagoon. Consequently, McCord's model is limited to situations where volatilization is controlled by the gas phase mass transfer. This limitation is similar to that of Mackay and Wolkoff's (1973) model. It has been shown by more recent research that most volatilization is liquid phase controlled. Additionally, McCord assumes that equilibrium at the air-water interface follows Raoult's law. However, for dilute aqueous solutions, the equilibrium should actually be determined on the basis of Henry's law.

AERATED IMPOUNDMENTS

Thibodeaux, Parker, Heck (1981d)

Thibodeaux, Parker and Heck (1981d) proposed use of their steady state model for nonaerated SIs for use with aerated impoundments with some modifications. The theory of two-film resistance is applicable to an aerated impoundment if one considers that turbulence, caused by aeration, creates two distinct zones at the impoundment surface; i.e., (1) turbulent, and (2) convective or natural. The overall liquid phase mass transfer coefficient for the entire system must be modified to account for each distinct zone, proportional to the affected area of each zone. The resulting overall K-value proposed by Thibodeaux, Parker and Heck for aerated SIs appears in Table 16.

As shown previously in Table 11, empirical relationships were developed by Thibodeaux, et al. to estimate individual liquid and gas phase k-values for a nonaerated (entirely convective zone) SI; i.e., $(k_L)_c$ and $(k_G)_c$, respectively. Similar relationships have also been experimentally developed to account for the turbulent zone caused by mechanical aeration. These empirical equations are shown below:

- **Individual liquid phase coefficient:**

$$(k_L)_T = \frac{J(\mathrm{POWR})(1.024)^{\theta-20}(\alpha)(10^6)}{165.04(a_v)(V)} \left(\frac{D_{i,H_2O}}{D_{O_2,H_2O}}\right)^{0.5}$$

TABLE 15. McCORD'S STEADY-STATE PREDICTIVE MODEL FOR NON AERATED SURFACE IMPOUNDMENTS

Model Form:

$$E_s = \frac{E_o L_s}{L_o}$$

where;

$$E_o = 0.53425\ A_m \left(\frac{D}{L}\right)^{0.22} (\%)\ (VP)\ (W_o)^{0.78}$$

$$L_s = \frac{K}{1-x}$$

$$1-x = \frac{E_o}{L_o} + \frac{F}{V}$$

$$K = 0.0834(F)\ (\%)\ (sp.gr.)$$

$$L_o = 0.0834(V)\ (\%)\ (sp.gr.)$$

Definition of Terms:

E_s = evaporation rate of a compound at steady state (lb/hr)
E_o = initial evaporation rate of a compound (lb/hr)
L_s = amount of compound in lagoon at steady state (lb)
L_o = initial amount of compound in lagoon (lb)
A_m = surface area of lagoon (m^2)
D = diffusivity coefficient of a compound in air (m^2/hr)
L = a lagoon dimension (m)
% = weight percent of compound in water or lagoon liquid
VP = vapor pressure of pure compound (atm)
W_o = wind velocity (m/sec)
K = amount of compound in feed stream (lb/hr)
F = feed rate (=discharge rate) in lagoon (gal/hr)
V = operating volume of lagoon (gal)
sp.gr. = specific gravity of liquid waste

TABLE 16. K-VALUES FOR AERATED SIs PROPOSED BY THIBODEAUX, PARKER AND HECK

$$K_L = (K_L)_c \frac{A_c}{A} + (K_L)_T \frac{A_T}{A}$$

where;

K_L = overall liquid phase mass transfer coefficient for the entire aerated surface impoundment (also termed the "area-averaged" coefficient) to be used in the basic model equation.

$(K_L)_c$ = overall liquid phase mass transfer coefficient

for the convective zone of the impoundment

$$\frac{1}{(K_L)_c} = \frac{1}{(k_L)_c} + \frac{1}{K(k_G)_c}$$

A_c = effective surface area of the convective zone

A = total surface area of the aerated impoundment ($A=A_T+A_c$)

$(K_L)_T$ = overall liquid phase mass transfer coefficient for the turbulent zone of the impoundment.

K = equilibrium constant

$$\frac{1}{(K_L)_T} = \frac{1}{(k_L)_T} + \frac{1}{K(k_g)_T}$$

A_T = effective surface area of the turbulent zone

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where:

J = oxygen-transfer rating of mechanical aerator (3 lb O_2/hr-hp);

POWR = total power input to aerators (hp)-rated hp x efficiency (0.65-0.9);

θ = temperature (°C);

α = oxygen-transfer correction factor (0.8-0.85);

a_v = surface area per unit volume of surface impoundment (ft^{-1});

V = volume of surface impoundment in region of effect of aerators (ft^3);

D_{i,H_2O} = diffusion coefficient of compound i in water (cm^2/sec);

D_{O_2,H_2O} = diffusion coefficient of oxygen in water (cm^2/sec)

- Individual gas phase coefficient:

$$(k_g)_T = 0.00039 \frac{\rho_g D_{i,\,air}}{d} (N_{Re})^{1.42} (N_{FR})^{-0.21} (N_p)^{0.4} (N_{Sc})^{0.5}$$

where:

ρ_g = density of the gas (lb/ft^3)

$D_{i,air}$ = diffusion coefficient of compound i in air (ft^2/hr)

d = diameter of aerator turbine or impeller (ft)

N_{Re} = gas Reynolds number = $\rho_g d^2 \omega/\mu g$

ω = rotational speed of turbine impeller (rad/sec)

μg = absolute gas viscosity (g/cm-sec)

N_{FR} = Froude number = $d\omega^2/g$

g = gravitational constant (32.17 ft/sec^2)

N_p = power number = $Pr\ g/\rho_L d^5 \omega^3$

Pr = power to the impeller ($ft-lb_f$/sec)

ρ_L = density of the liquid (lb/ft^3)

N_{Sc} = gas schmidt number = $\mu g/\rho_g D_{i,\,air}$

Note: N_{Sh} = Sherwood number = $(k_g)_T\ d/\rho_g D_{i,air}$

and therefore, $N_{Sh}=0.00039(N_{Re})^{1.42}(N_p)^{0.4}(N_{Sc})^{0.5}/(N_{FR})^{0.21}$

Freeman (1979), working with surface aerated waste treatment basins, has tabulated values published in the literature for estimating; (1) effective surface area of the turbulent zone (A_T); (2) surface area per unit volume of surface impoundment (a_v); and (3) volume of surface impoundment in region of effect of aerators (V), based on the mechanical aerators horsepower, ω. These parameters are shown in Table 17.

As discussed in the preceeding section, several other researchers have shown that the individual mass-transfer coefficients for various compounds in a nonaerated impoundment (convective zone coefficients) can be simplified by comparison to a typical compound. This simplification process has been applied for determining the individual mass transfer coefficients from the turbulent zone of an aerated impoundment as shown below:

- Individual liquid phase coefficient:

$$(k_{L,i})_T = \left(\frac{MW_{O_2}}{MW_i}\right)^{0.25} \left(\frac{1.024^{\theta-20}}{1.024^5}\right) \left(\frac{273+\theta}{298}\right)^{0.5} \left(k_{L,O_2}\right)$$

- Individual gas phase coefficient:

$$(k_{G,i})_T = \left(\frac{MW_{H_2O}}{MW_i}\right)^{0.25} \left(\frac{298}{273+\theta}\right)^{0.92} \left(k_{G,H_2O}\right)$$

However, as noted previously, a key limitation to this simplification procedure is that the values of k_{L,O_2} and k_{G,H_2O} are best determined by using the complex empirical relationships shown earlier.

McCord (1981)

One additional predictive model was proposed by McCord (1981) to estimate the emission rate of volatile compounds from aerated lagoons. This steady-state model, based upon Arnold's (1944) studies on the diffusion of volatile compounds from a liquid surface into air, appears in Table 18.

Discussions in the preceeding section concerning McCord's steady-state predictive model for nonaerated impoundments showed that the basis for McCord's model is evaporation of water from the impoundment surface; i.e., gas phase controlling. Therefore, in reality, this model does not accurately represent the volatilization rate of most sparingly (slightly) soluble volatile organic compounds.

TABLE 17. TURBULENT AREAS AND VOLUMES FOR SURFACE AGITATORS[a]

ω, Motor horsepower, hp	A_T, Turbulent area, ft^2	Effective depth, ft	V, Agitated volume, ft^3	a_V, Area per volume ft^2/ft^3
5	177	10	1,767	0.100
7.5	201	10	2,010	0.100
10	227	10.5	2,383	0.0952
15	284	11	3,119	0.0909
20	346	11.5	3,983	0.0870
25	415	12	4,986	0.0833
30	491	12	5,890	0.0833
40	661	13	8,587	0.0769
50	855	14	11,970	0.0714
60	1,075	15	16,130	0.0666
75	1,452	16	23,240	0.0625
100	2,206	18	39,710	0.0555

[a] Data for a high speed (1,200 rpm) aerator with 60 cm propeller diameter (d).

TABLE 18. McCORD'S STEADY-STATE PREDICTIVE MODEL FOR AERATED SIs

Model Form:

$$E_s = \frac{E_o \, L_s}{L_o}$$

where;

$$E_o = \frac{150.315}{(460 + T)} \; \frac{H}{r} \; \frac{L_o}{V_L} \; \frac{VP}{\text{sp. gr.}} \; \frac{d}{\pi} \; \frac{1}{\sqrt{0.17678R^{1/2}}}$$

$$L_s = \frac{K}{1-x}$$

$$1-x = \frac{E_o}{L_o} + \frac{F}{V}$$

$$K = (0.0834)(F)(\%)(\text{sp.gr.})$$

$$L_o = (0.0834)\,(V)\,(\%)\,(\text{sp. gr.})$$

Definition of Terms:

E_s = evaporation rate of a compound at steady-state conditions (lb/hr)

E_o = initial evaporation rate of a compound (lb/hr)

L_s = pounds of a compound in the lagoon at steady-state conditions

L_o = initial pounds of a compound in the lagoon

T = temperature (°F)

H = amount of water delivered by the aeration pump (gpm)

r = radius of spherical drops emitted (cm)

V_L = volume of liquid waste in lagoon (U.S. gal)

VP = vapor pressure of the volatile compound at temperature T (atm)

sp. gr. = specific gravity of the liquid waste

d = diffusivity coefficient of a compound in air (cm^2/sec)

(continued)

TABLE 18 (continued)

R = maximum diameter of the aeration spray falling back into the lagoon (m)

K = amount of compound in the feed stream (lb/hr)

F = feed rate (= discharge rate) in lagoon (gal/hr)

V = operating volume of lagoon (gal)

% = weight percent of a compound in water or lagoon liquid

SECTION 5

REVIEW OF LANDFILL AERR MODELS

INTRODUCTION

Six air emission modeling equations were presented in the literature for landfill facilities:

- Three models for covered landfills without internal gas generation (Farmer, Shen, Thibodeaux); and
- One model for each of the following scenarios: (1) covered landfills with internal gas generation (Thibodeaux); (2) covered landfills with gas generation and barometric pumping effects (Thibodeaux); and (3) uncovered landfills (Shen).

This section presents all models for landfills found in the literature. Tables 19 and 20 respectively summarize available model equations for landfills and the necessary input parameters required for each equation. GCA's recommendations for landfill models and mass transfer coefficients were presented previously in Section 2.

Two of the three AERR equations for covered landfills without internal gas generation were based on laboratory studies conducted by Farmer, et al., (1978). Shen (1980) modified Farmer's equation by changing the flux rate to an emission rate by multiplying by the landfill surface area. In addition, to determine the AERR for a specific component of the waste, Shen multiplies the emission rate by the weight fraction of that component in the bulk waste. Details of both models are provided in this section.

Farmer's laboratory experiments assumed the vapor release of hexachlorobenzene (HCB) was diffusion controlled within the soil phase because of HCBs insolubility in water (i.e., not effected by water movement) and HCBs resistance to biological activity. However, Thibodeaux's (1981a) equation takes on a similarity of the two-resistance theory of mass transfer. Thibodeaux not only describes the vapor movement within the soil phase (as does Farmer), but also addresses the vapor movement from air-soil interface to the overlying air. In practice, the air-soil interface transfer should provide negligible resistance, and thus can be disregarded.

TABLE 19. REVIEW OF AVAILABLE AERR LANDFILL MODELS[a]
(AS PRESENTED IN THE LITERATURE)

A. Farmer, et al. (1978) for covered landfills:

(1) $J = D_o \left(P_a^{10/3}/P_T^{2}\right)(C_s - C_2)/L$

(2) $D_A = D_B \left(\frac{M_B}{M_A}\right)^{1/2}$

(3) $C_s = P^o \frac{M}{RT}$

(4) $P_a = P_T - \theta$

(5) $P_T = 1 - \frac{\beta}{\rho}$

(6) $\theta = \frac{\omega\beta}{\rho_\omega}$

B. Shen's (1980) Modification of Farmer's Equation:

(1) $E_i = D_i \; C_{si} \; A \; P_T^{4/3} \left(\frac{1}{L}\right)\left(\frac{W_i}{W}\right)$

(2) $D_i = D_A = D_B \left(\frac{M_B}{M_A}\right)^{1/2}$

(3) $C_{si} = C_s = \frac{P^o M}{RT}$

(4) $P_T = 1 - \frac{\beta}{\rho}$

C. Thibodeaux's (1981a) Landfill Equation--Without Internal Gas Generation:

(1) $N_A = {}^1K_{A3} \left(\rho^*_{A1} - \rho_{A1}\right)$

(2) $N_A = N_{A\text{ soil}} + N_{A\text{ air-soil}}$

(continued)

TABLE 19 (continued)

(3) $N_{A_{soil}} = \frac{D_{A3}}{h} (\rho^*_{Ai} - \rho_{A1i})$

(4) $N_{A\ air\text{-}soil} = {}^3K_{A1} (\rho_{A1i} - \rho_{A1})$

(5) $D_{A3} = D_{A1} \frac{\varepsilon}{\tau}$

(6) $\frac{1}{{}'K_{A3}} = \frac{1}{{}'K_{A3}} + \frac{1}{{}^3K_{A1}}$

D. Thibodeaux's (1981a) Landfill Equation--With Internal Gas Generation

(1) $N_A = V_y \frac{(\rho^*_{A1} - \rho_{A1i})}{\exp (h\ V_y/D_{A3}) - 1} + V_y\ \rho^*_{Ai}$

(2) $\rho_{A1} = \rho^*_{A1} - (\rho^*_{A1} - \rho_{A1i}) \frac{1 - \exp (y\ V_y/D_{A3})}{1 - \exp (h\ V_y/D_{A3})}$

E. Thibodeaux, et al. (1981b) Landfill Equation With Internal Gas Generation and Barometric Pumping:

(1) $N_A = \frac{D_{A3}}{L}\ \rho^*_{AL}\ \frac{R \exp R}{\exp R\text{-}1}$

(2) $R = \frac{LV}{D_{A3}}$

(3) $V = \frac{K}{\mu L} (P - \pi)$

F. Shen's (1980) Open Dump Equation:

(1) $\frac{dV}{dt} = 2\ C_e\ \omega \sqrt{\frac{DLV}{\pi\ Fv}}\ \frac{W_i}{W}$

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[a] Definition of terms appears in Table 20.

TABLE 20. INPUT PARAMETERS REQUIRED FOR EACH LANDFILL MODEL IN TABLE 19

Parameter	Model					
	A	B	C	D	E	F
J, vapor flux through soil	X					
D_o, diffusion coeff. in air	X	X				
C_s, conc. material in air	X	X				
C_2, conc. of material at soil surface	X	X				
L, soil depth	X	X				
P_a, soil air filled porosity	X	X				
P_T, total soil porosity	X	X	X			
D_A, air diffusion coeff. for unknown compound	X	X				
D_B, air diffusion coeff. for known compound	X	X				
P^o, vapor pressure	X	X				
M, molecular weight	X	X				
R, molar gas constant	X	X				
T, absolute temperature	X	X				
β, soil bulk density	X	X				
ω, gravimetric soil water content	X	X				
ρ_ω, density of water	X	X				
ρ, particle density	X	X				
W_i/W, weight % of component i in bulk waste		X				
E_i, emission rate of vapor i		X				
N_a, mass flux rate			X	X	X	

(continued)

TABLE 20 (continued)

Parameter	Model A	 B	 C	 D	 E	 F
${}^1K_{A3}$, overall soil phase transfer coeff.			X			
ρ^*_{A1}, conc. of A in sand chamber filled pore spaces			X	X		
ρ_{A1}, conc. of A in air at distance from air-soil interface			X	X	X	
N_A, rate of vapor movement within soil phase			X	X	X	
h, depth of fill cover			X	X		
D_{A3}, effective diffusivity of A within the air-filed soil pore space			X	X	X	
D_{A1}, molecular diffusivity of A in air			X			
τ, tortuosity			X			
${}^3k_{A1}$, gas phase mass transfer coeff.			X			
V_x, wind speed at 10 m			X			
L, length of ground emission source			X			
V_y, mean gas velocity in pore spaces				X		
ρ_{A1i}, conc. of A at air-soil interface				X		
L, cap thickness					X	
V, superficial velocity through cap					X	
K, permeability of cap material					X	
μ, cell gas velocity					X	
P, cell gas pressure					X	

(continued)

TABLE 20 (continued)

Parameter	Model A	B	C	D	E	F
π, atmospheric pressure					X	
$\frac{dV}{dt}$, volume conc. of vapor						X
C_e, equilibrium vapor conc.						X
ω, width of open dump						X
V, wind speed						X
F_v, correction factor						X

Thibodeaux (1981a) presents another model describing vapor movement in soil which is subject to the effects of biogenic processes and related gas generation. This "sweeping" action provided by the upward movement of landfill gases provides a parallel transfer motion to the molecular diffusion of vapor in the soil phase.

Thibodeaux (1981b) further developed his model to include the barometric pumping effect caused by fluctuations in atmospheric pressure and landfill cell pressure. Computer simulation tests indicated that the flux rate of benzene, N_A, is influenced only slightly by barometric pressure fluctuations under conditions of co-disposal, and influenced significantly under conditions of no internal gas generation (i.e., no co-disposal with municipal refuse).

This statement suggests that for a co-disposal facility, Thibodeaux's model for landfills with gas generation should be employed. For a landfill handling strictly hazardous waste, with no expected internal gas generation, either of two models (Farmer, or Thibodeaux) may be appropriate. However according to Springer (1983), the effect of barometer pumping is not reversible and will not average out over a long period of time. An increase of 10 to 15 percent to emission release rate could be expected.

To determine AERR from an uncovered landfill, Shen (1981) presents the equation based on Fick's Law. This is the only open dump AERR model presented in the literature and it assumes an insoluble material with vapor movement that is only air-phase controlled. A review of Thibodeaux's two-resistance-landfill equation, specifically the rate of vapor movement from the air-soil interface to overlying air (air-phase resistance) indicates it may be a more accurate description of vapor movement in the gas phase because it accurately accounts for wind effects across the earth's boundary i.e., Sutton (1953). Further development for the open dump case may be warranted.

FARMER, ET AL. (1978) FOR COVERED LANDFILLS

The equation developed by Farmer was intended as a method of assisting a planner in designing a landfill cover that minimized the escape of hexachlorobenzene (HCB) or other volatile organic vapors. Alternatively, the equation could be used to assess the effectiveness of an existing landfill cover for controlling organic vapor flux to the atmosphere. The equation was experimentally verified by Farmer for HCB-containing waste in a laboratory-simulated landfill.

Using Fick's First Law for steady-state diffusion, Farmer describes the volatilization or vapor loss of HCB, or other compounds, as a diffusion controlled process. With the assumptions of no degradation from biological activity, no adsorption of the compound, no transport in moving water and no landfill gas production, the rate at which a compound will volatize from the soil surface to the atmosphere will be controlled by the diffusion rate through the soil cover. To describe molecular diffusion through a soil surface, Farmer adopted the effective diffusion coefficient suggested by Millington and Quirk (1961) as shown below:

$$D_e = D_o\left(\frac{P_a^{10/3}}{P_T^{2}}\right)$$

where: D_e = effective diffusion coefficient in soil;

D_o = diffusion coefficient in air;

P_a = soil air-filled porosity;

P_T = total porosity.

This equation describes the effective diffusion coefficient as a power function of soil porosity. This method may be valid, however, as described previously in Section 2, additional research indicated the power function may be soil-type dependent. Thus, this equation appears to be limited to the soil class with which Millington and Quirk experimented with, namely isotropic soil.

The following describes the methods employed by Farmer (1980) to determine equation parameters, and identifies some simplifications to the overall equation.

A. Diffusion coefficients, D_o, are available for many compounds, generally at a specified temperature. The vapor diffusion coefficient for an unknown compound A can be estimated from a known compound (B) by the following equation:

$$D_A = D_B\left(\frac{M_B}{M_A}\right)^{1/2}$$

where M_A, M_B = molecular weights of compounds A and B, respectively.

To determine the diffusion coefficient at a temperature other than a temperature listed, the following equation can be used:

$$D_2 = D_1\left(T_2/T_1\right)^{1.5}$$

where D_1 and D_2 are the diffusion coefficients at temperatures T_1 and T_2, respectively.

B. Saturation vapor density at the bottom of the soil layer, C_S, can be obtained based on the ideal gas law:

$$C_S = P^oM/RT$$

where: P^o = vapor pressure (mm Hg);

M = molecular weight (g/g-mole);

R = molar gas constant (62.36 l-mm Hg/°K-mole)

T = absolute temperature (°K)

Farmer experimented with pure HCB, thus, he calculated the pure component vapor concentration. For mixtures, the vapor concentration of a component in the waste becomes the driving force and this is not equal to the saturation vapor concentration of the pure component. The vapor concentration for a component in a waste mixture is calculated by:

$$C_i^* = \frac{P_i^* M}{RT}$$

where P_i^* = partial pressure of component i in the waste mixture.

The partial pressure in a liquid mixture is determined as follows:

$$P_i^* = \gamma_i P^o X_i$$

where: γ_i = activity coefficient of component i; and

X_i = mole fraction of component i in the liquid.

For hydrocarbon mixtures, $\gamma_i = 1$, but for aqueous mixtures the activity coefficient must be determined.

C. Soil air-filled porosity, P_a, is calculated from the total porosity, P_T, and the volumetric soil water content, θ, where

$$P_a = P_T - \theta$$

and

$$\theta = W\beta/\rho_w$$

where: W = gravimetric soil water content (g/g);

β = soil bulk density (g/cm^3);

ρ_w = density of water = 1 g/cm^3.

A worst-case assumption would be completely dry soil, thus, $P_a = P_T$, and the flux equation becomes

$$J = D_o P_T^{4/3} \left(C_S - C_2\right)/L$$

The addition of any water to the soil will reduce the air-filled porosity, thus, reduce vapor flux from the soil surface because the diffusion rate through a liquid is generally several magnitudes less than diffusion through air.

D. The total soil porosity, P_T, can be calculated from the soil bulk density, ß, by the following equation:

$$P_T = 1-\beta/\rho$$

where: ß = soil bulk density (g/cm^3);

ρ = particle density (g/cm^3).

Particle density is usually taken as 2.65 g/cm^3 for most soil mineral material, while soil bulk density usually varies from 1.0-2.0 g/cm^3. Therefore, P_T can range from 0.245 to 0.623 cm^3/cm^3, and $(P_T)^{4/3} = 0.153$ to 0.532.

Worst-case scenario would be $P_T{}^{4/3} = 0.532$ (from ß = 1.0 g/cm^3), thus $J = 0.532\ D_o\ (C_S-C_2)/L$. This flux rate equation would allow for a worst case estimate of air emissions.

E. Farmer assumed that the concentration of volatilizing material at the soil surface, C_2, is zero. The reasons for this assumption were stated by Farmer as:

1. the amount of vapor reaching soil surface will be very small; and

2. the vapor will be rapidly dispersed by wind currents and by diffusion in air. Thus, the simplified version of Farmer's equation becomes:

$$J = D_o\ P_T{}^{4/3}\ C_S/L$$

The assumption of $C_2 = 0$, implies worst-case situation because any increase in C_2 will effectively reduce the concentration gradient (driving force behind vapor flux) and reduce vapor flux from soil surface.

SHEN'S (1980) MODIFICATION OF FARMER'S EQUATION

Basically, Shen took the simplified version of Farmer's equation for vapor flux from a soil surface and converted to an emission rate by multiplying by the exposed area. To determine the emission rate of a specific waste, component i, Shen multiplied by the weight percent of component i in the bulk waste (Wi/W). However, weight percent should be replaced by mole fraction. Additionally, in calculating the emission rate of a specific compound in a waste mixture, consideration of waste composition and the activity coefficient is important. This procedure was previously outlined.

Since both Farmer's and Shen's equations are nearly identical, the parameters D_i, C_{si}, and P_T can be calculated and simplified in similar manners. For illustrative purposes, Table 21 presents typical parameter values and ranges for the modified landfill equation.

TABLE 21. TYPICAL PARAMETER VALUES AND RANGES FOR THE FARMER LANDFILL MODEL AS MODIFIED BY SHEN

Equation 1: $E = D\,C_s\,A\,P_t^{4/3}\,\frac{1}{L} \times \frac{W_i}{W}$ Equation 2: $D_i = D_K \left[\frac{M_K}{M_i}\right]^{0.5} \left|\frac{T}{T_K}\right|^{1.5}$ Equation 3: $C_s = \frac{PM}{RT}$ Equation 4: $\dot{P}_t = 1 - \frac{B}{\rho}$

Symbol	Units	Definition	Source of input parameter	Typical value	Expected range	Comments
D	cm^2/sec	Diffusion coeff.	Calc. from Eq. 2	NA	10^{-1}-10^{-3}	Methanol high at 0.157; trichloroethylene low at 0.0525 @ 20°C
C_s	g/m^3	Saturation vapor conc.	Calc. from Eq. 3	NA	10^{-3}-10^{-5}	Methyl chloride high at 2.39 x 10^{-3}; benzene low at 3.0 x 10^{-5}
A	cm^2	Surface area	Measured or typical value assumed	100 m^2	25-5,000 m^2	Highly variable parameter
P_t	Dimensionless	Soil porosity	Calc. from Eq. 4	0.43	0.25-0.62	
L	cm	Depth of soil cover	Measure or typical value assumed	30	25-35	
W_i/W	g/g	Weight fraction of chem.	Measure or typical value assumed	2%	0.5-5%	Highly variable parameter
D_K	cm^2/sec	Known D of ref. compound	Chemical handbook			
M_K	g/mole	MW of ref. compound	Chemical handbook	NA	50-190	For organic compounds, chloromethane is low @ 51, PCB is high @ 189
M_i	g/mole	MW of compound	Chemical handbook	NA	50-190	For organic compounds, chloromethane is low @ 51, PCB is high @ 189
T	°K	Temperature	Measured or typical value assumed	292	250-310	Highly variable parameter
P	mm Hg	Vapor pressure	Chemical handbook	NA	0.02-750	PCB low at 0.015, Cyclohexane high at 721
R	$\frac{\text{mm Hg-liter}}{\text{°K-mole}}$	Gas constant	Chemical handbook	62.36	NA	Constant value
B	g/cm^3	Soil bulk density	Soil handbook	1.5	1-2	
ρ	g/cm^3	Particle density	Soil handbook	2.65	2.4-2.8	ρ = 2.65 for most mineral matter

THIBODEAUX'S (1981a, 1981b) LANDFILL EQUATIONS

Thibodeaux (1981a, 1981b) presented three equations for estimating air emissions from covered landfills; (1) without internal gas generation, (2) with internal gas generation, and (3) with internal gas generation including the effect of barometric pumping pressure.

Without Internal Gas Generation

Thibodeaux's equation for covered landfills without gas generation appears similar to the two resistance theory of mass transfer: i.e., Flux = (overall transfer coefficient) (concentration gradient). The equation is the algebraic sum of the two individual phase equations; the rate of vapor movement within the soil phase, and rate of vapor movement from air-soil interface to overlying air.

The rate controlling portion of Thibodeaux's flux rate equation is the rate of vapor movement within the soil phase. The mass transfer coefficient for vapor diffusion in soil is described for vapor movement through a porous media. However, other research previously presented in Section 2 indicates that a more correct expression is to show the effective diffusivity dependency upon a power function of porosity. This power is a function of soil type and moisture content. The second portion of Thibodeaux's equation describes the vapor movement through air, based on the work of Sutton (1953).

With Internal Gas Generation

In addition to molecular diffusion of landfill vapors through soil, there is a "convective sweep" of chemical vapors toward the surface created by the formation of landfill gases (CO_2, H_2, CH_4), especially applicable to co-disposal sites. Therefore, the flux equation contains both a diffusive and convective term.

Barometric Pumping Effects

Additional work by Thibodeaux, Springer and Riley (1981b) addressed a third vapor phase transport mechanism in addition to the diffusive and convective mechanisms previously discussed; the barometric pumping pressure. Atmospheric pressure fluctuations develop pressure gradients which pump vapors and gases from landfill cells to the air above. This pumping enhances vapor phase mass transfer.

Changes in barometric pressure will correspondingly change R (see Equation E-2, Table 19) to a positive, zero, or negative value (thus effecting flux rate). For instance:

for $< \pi$, R 0 (air inflow): N_A is suppressed (= 0).

$p = \pi$, $R = 0$: $N_A = D_{A3}\overset{*}{\rho}_{A1}/L$ (rate of vapor movement in soil without gas generation--see Thibodeaux's previous equation)

$p > \pi$, $R > 0$ (air outflow): N_A is increased due to pressure gradient driving force.

It was also shown that cell gas pressure, p, will vary with time and is dependant upon gas generation and the cyclic behavior of fluctuating atmospheric pressures, such that:

$$\frac{dp}{dt} = \frac{r_B \rho_W p}{\varepsilon_c} - \frac{Kp(p - \pi)}{\varepsilon_c h_c L \mu}$$

where: r_B = biogas generation rate (cm^3/g-sec);

ρ_W = bulk density of waste (g/cm^3)

p = cell gas pressure (atm);

ε_c = cell porosity;

K = permeability of cap material (cm^2-cp/sec-atm);

π = atmospheric pressure (atm);

h_c = cell depth (cm)

L = cap thickness (cm)

μ = cell gas viscosity (cp)

Computer simulation tests indicated that the flux rate of benzene, N_A, is influenced only slightly by barometric pressure under conditions of co-disposal (gas generation) and influenced significantly by barometric pressure under conditions of no internal gas generation. The air emissions model equations which incorporate factors for gas generation (and their related effects on flux rate) should be applied for situations of co-disposal.

SHEN'S (1980) OPEN DUMP EQUATION

The emission rate equation for open dumps presented by Shen is derived from Fick's Law and Arnold's (1944) equation for a surface exposed to open air. A major limitation of this model is that it only considers air-phase diffusion and it does not accurately describe the effect of boundary layer formation caused by ambient wind, as shown by Thibodeaux in describing the gas-phase resistance of vapor movement. This limitation suggests further development of this model is appropriate.

SECTION 6

REVIEW OF LAND TREATMENT AERR MODELS

INTRODUCTION

The technical literature contains two models for calculating air emission release rates (AERR) from landfarming (land treatment) operations. Table 22 summarizes the available equations for land treatment facilities, showing the input parameters required for each model. Table 23 presents typical parameter values and ranges for the Thibodeaux-Hwang (1982) AERR model.

The Thibodeaux-Hwang (1982) model most accurately defines the physical situation existing in a landfarm, namely the mass transfer of a chemical species from a soil-waste mixture. One apparent limitation to this model is that it decribes vapor diffusion as being soil-phase controlled, based on the assumption that the oil-layer diffusion length is on the order of a soil particle size. This assumption may only be valid after a certain exposure time. For petroleum waste, the sludge material generally subjected to landfarming is a multicomponent viscous material. Molecular diffusion coefficients for this material may be several orders of magnitude less than that for soil-phase diffusion. Thus, the diffusion rate determining factor will be the application thickness of the waste material. Additionally, it may be possible that both phases (soil and oil) will contribute equally to the diffusion rate of a specific component.

THIBODEAUX-HWANG: MODELING AIR EMISSIONS FROM LANDFARMING OF PETROLEUM WASTES (1982)

With the assumptions that the soil column is isothermal, that no vertical movement of waste occurs by capillary action, no adsorption of material occurs on soil particles and that no biochemical oxidation occurs, the Thibodeaux-Hwang model describes the vapor movement of a chemical species from a soil-waste mixture. This model is applicable to either surface application or subsurface injection methods of landfarming.

The one key variable in the Thibodeaux-Hwang derivation appears to be the oil-layer diffusion length, Z_o. This term is related to application rate of oil waste and thus its value will determine the extent that oil-phase diffusion will play an important role in the flux rate determination. The simplified version of the Thibodeaux-Hwang model assumes a low value for

TABLE 22. INPUT PARAMETERS REQUIRED FOR EACH LAND TREATMENT AERR MODEL

Parameter	Thibodeaux - Hwang[a]	Hartley[b]
D_{ei}, diffusivity of i in air filled pore spaces	X	
D_{ai}, molecular diffusivity of i in air	X	
D_{wi}, diffusivity of i in waste oil	X	
Z_o, oil-layer diffusion length	X	
A_s, interfacial area per unit volume of soil	X	
ε, soil porosity	X	
τ, tortuosity	X	
h_s, depth of surface injection	X	
A, surface area of application	X	X
h_p, depth of penetration or plow slice depth	X	
M_{io}, initial mass of component i	X	
t, time	X	
C_{ig}, concentration of i on gas side of interface	X	
H_c, Henry's Law constant in concentration form	X	
C_{il}, concentration of i in oil phase	X	
H, Henry's Law constant	X	
C_g, molar density of vapor	X	
P, total pressure	X	
δ, soil bulk density	X	
ρ, particle density	X	
E_w, water evaporation rate		X
RH, relative humidity		X
P_a, vapor pressure of chemical		X
P_w, vapor pressure of water		X
M_a, molecular weight of chemical		X
M_o, modelucar weight of water		X
Wi/W, weight fraction of chemical in the waste		X

[a] Thibodeaux - Hwang:

(1) $q_i = D_{ei} C_{ig}/[h_s^2 + (2 D_{ei} t A (h_p - h_s) C_{ig})/M_{io}]^{1/2}$

(2) $D_{ei} = D_{ai} \varepsilon/\tau$

(3) $\varepsilon = 1 - \beta/\rho$

(4) $$C_{ig} = \left[\frac{H_c}{1 + \left(\frac{6 D_{ei} Z_o H_c}{D_{wi} a_s (h_p^2 + h_p h_s - 2h_s^2}\right)}\right] C_{iwo}$$

(5) $H_c = HC_g \frac{10^6}{P}$

[b] Hartley:

(1) $$E_a = \frac{E_w}{(1-RH)} \times \frac{P_a (M_a)^{1/2}}{P_w (M_w)^{1/2}} \times A \times \frac{W_i}{W}$$

TABLE 23. TYPICAL PARAMETER VALUES AND RANGES FOR THE THIBODEAUX-HWANG LAND TREATMENT AERR MODEL

Symbol	Units	Definition	Source of input parameter	Typical value	Expected range	Comments
q_i	g/cm^2-sec	flux rate	calculated from equation 1[a]	-----	-----	-----
D_{ei}	cm^2/sec	diffusivity of i in air-filled pore spaces	calculated from equation 2[b]	-----	-----	-----
D_{ai}	cm^2/sec	molecular diffusivity of i in air	chemical handbook or calculated from reference chemical	10^{-1}	10^{-3}	Highly variable input parameter
ϵ	dimensionless	soil porosity	calculated from equation 3[c]	0.43	0.25 - 0.62	
τ	dimensionless	tortousity	constant value	$\overline{3}$	N.A.	$\overline{3}$ is a constant value (assumed)
h_s	cm	depth of surface injection	measured on typical value assumed	0	0 - 20 cm	hs = 0 for surface application
A	cm^2	surface area of application	measured	N.A.	(3-10) x 10^7	highly variable input parameter
h_p	cm	depth of penetration or plow slice depth	measured or typical value assumed	19	8 - 30	value of hp subscript may be low shortly after surface application
M_{io}	g	initial mass of component i	measured	N.A.	N.A.	-----
t	sec	time after application	measured	N.A.	0-5 x 10^6	-----
C_{ig}	g/cm^3	concentration of i on gas side of interface	calculated from equation 4[d]	N.A.	N.A.	-----
H_c	cm^3 oil/ cm^3 air	Henry's Law Constant in concentration form	calculated from equation 5[e]	N.A.	N.A.	-----
C_{il}	g/cm^3	conc. of i in oil phase	measured	N.A.	N.A.	highly variable parameter
H	atm-m^3/mol	Henry's Law Constant	chemical handbook	N.A.	10^{-3} - 10^{-5}	highly variable parameter
C_g	g-mol/cm^3	molar density of vapor	use typical value or calculate (see comments)	1/2.44 x 10^4	N.A.	$C_g = \frac{p°}{RT}$

(continued)

TABLE 23 (continued)

Symbol	Units	Definition	Source of input parameter	Typical value	Expected range	Comments
P	atm.	total pressure	measured or typical value assumed	1	0.7 - 1	standard atm. pressure is 1 atm
B	g/cm^3	soil bulk density	soil handbook	1.5	1 - 2	
ρ	g/cm^3	particle density	soil handbook	2.65	2.4 - 2.8	ρ = 2.65 for most mineral matter

[a]Equation 1. $q_i = D_{ei} C_{ig}/[h_s^2 + (2 D_{ei} tA(h_p - h_s)C_{ig})/M_{io}]^{1/2}$

[b]Equation 2. $D_{ei} = D_{ai}\, \epsilon/\tau$

[c]Equation 3. $\epsilon = 1 - B/\rho$

[d]Equation 4:

$$C_{ig} = \left[\frac{H_c}{1 + \left(\frac{6\, D_{ei}\, Z_o\, H_c}{D_{wi}\, a_s\, (h_p^{\,2} + h_p h_s - 2h_s^{\,2})}\right)}\right] C_{iwo}$$

[e]Equation 5. $H_c = HC_g\left(\frac{10^6}{P}\right)$

Z_o, i.e., soil particle size thickness, thus for all cases that make use of this assumption Equation (4) from Table 22 becomes:

$$C_{ig} = H_c C_{iL}$$

C_{ig} = concentration of component i in gas phase;

H_c = Henry's Law constant (concentration form);

C_{iL} = concentration of component i in oil phase.

Thibodeaux and Hwang also present a flux rate equation which identifies the air emission release rate immediately after waste application:

$$q_i = k_g C_i^*$$

where: q_i = flux rate (g/cm^2-s);

k_g = gas-phase mass transfer coefficient (cm/s);

C_i^* = vapor concentration of chemical i (g/cm^3).

This equation assumes no mass-transfer resistance in the soil phase and thus is applicable only for short periods of time (i.e., immediately after application, or for spills, and while a liquid pool is still visible). More importantly, the equation is only valid for a pure compound because it provides no description of liquid-phase resistance. Here again the application thickness will be a controlling variable. For use in describing air emission release rates of a waste material, it is more correct to use an overall mass-transfer coefficient. Refinement of this equation may generate a method of quantifying air emissions from drum storage facilities.

This short term emissions estimate model closely correlates to the flux rate model described by Hartley. The Hartley model does not accurately describe the physical situation of land application as described later.

There is little experimental data available which can be used to validate this model in either its complete or simplified forms. The apparent good agreement with dieldrin test data as shown by Thibodeaux and Hwang (1982) may not represent true field conditions.

HARTLEY MODEL (1969)

The Hartley model was developed to determine the evaporative loss of pure volatile compounds. Although it is applicable to land spreading operations, it is not applicable to landfarming methods. The model assumes that the rate of mass transfer is controlled by resistance in the gas phase and is proportional to the saturated vapor concentration. The liquid phase resistance, which plays an important role for multicomponent liquid mixtures containing volatile compounds, is completely ignored in the model development.

Simply stated, the Hartley model calculation of the flux rate of a chemical compound is performed on the basis of a known flux rate of a reference compound. Water is generally taken as the reference compound.

Although the Hartley model represents a simple method of calculating air emission release rate of chemical compounds from a soil surface (or any surface), it does not accurately represent air emission release rates of landfarming application as does the Thibodeaux-Hwang model. Several drawbacks to the Hartley model include:

- predicts a maximum emission rate throughout volatilization period;
- doesn't account for incorporation of volatile material within soil;
- not readily extended to complex, multicomponent mixtures;
- based on a nonvolatile reference compound (water).

SECTION 7

STORAGE TANK AIR EMISSION ESTIMATION TECHNIQUES

INTRODUCTION

Air emissions of volatile compounds from storage tanks at TSDFs are a function of several factors including:

- physical and chemical characteristics of the stored liquid;
- tank design;
- tank condition and site conditions; and
- operational characteristics, especially turnover frequency.

For a given liquid, tank design influences the emission rate potential. The five types of storage tanks, which are described later in this section, are:

- fixed roof;
- external floating roof;
- internal floating roof;
- variable vapor space; and
- pressure tanks.

Of the five designs, variable vapor space and pressure tanks generally produce the least air emissions.

In addition to tank design, the true vapor pressure of the material stored is one of the most significant parameters affecting emissions. Consequently, the type of tank selected during plant design is partially dependent on the vapor pressure of the material being stored. According to Erickson (1980), fixed roof tanks are preferred for storing materials with vapor pressures up to 34.5 kPa (5 psia); floating-roof tanks when vapor pressures are in the range of 6.9 to 34.5 kPa (1 to 5 psia); and pressure tanks when vapor pressures are greater than 51.7 kPa (7.5 psia). Other factors such as material stability, safety hazards, health hazards, and multiple use also influence tank selection for a particular organic liquid.

Physical actions on the tank such as changes in temperature or pressure affect the volatilization rate. Temperature increases from direct solar radiation and contact with warm ambient air increase volatilization and emission potential. Danielson (1973) notes that for a free vented tank, winds may entrain or educt some of the saturated vapors into the ambient air.

Operating conditions also affect storage tank emissions; i.e., frequency of filling (turnover rate), vapor tightness of the tank, and volume of the vapor space. Fixed-roof tanks maintained completely full limit the volume of vapor space and, thus, emissions. When the turnover rate is long; i.e., extensive time periods between filling/emptying cycles, the free space in a tank becomes more saturated with vapor from the liquid. Thus, during filling of the tank or during breathing cycles, a larger concentration of vapors exists in the air-vapor mixture vented to the atmosphere. Danielson (1973) states that vapor tightness of the tank can influence the evaporation rate, and a lack of tight vapor seal allows increased emissions. Proper seal maintenance for floating tanks is necessary to limit vapor losses.

The American Petroleum Institute (API), EPA and others have developed empirical equations for fixed and floating roof tank emissions based on field test data. Masser (1981) notes that emissions from pressure tanks occur only when the design pressure is exceeded, when the tank is filled improperly, or when abnormal vapor expansion occurs. Because these are not regularly occurring events, and pressure tanks are not a significant source of emissions under normal operating conditions, no equations were found available for estimating air emissions from pressure tanks.

Table 24 summarizes the recommended equations for fixed and floating roof tanks, showing the input parameters required for each model. Following sections describe these models in more detail, and also describe additional, non-recommended models found in the literature. Special case consideration for open tanks and storage of mixtures is also presented.

FIXED ROOF TANKS

A typical fixed roof tank is shown in Figure 7. Air emissions from fixed roof tanks occur from breathing losses and working losses. Masser (1981) defines breathing loss (L_B) as vapor expulsion due to vapor expansion and contraction from changes in tank temperature and ambient barometric pressure. Breathing losses occur in the absence of any liquid level change in the tank.

The combined loss from periodic filling and emptying is called working loss (L_W). When a tank is filled, vapors are expelled from the tank when the pressure inside the tank causes opening of the relief valve. Emptying loss occurs when air drawn into the tank during liquid removal becomes saturated with organic vapor, expands, and exceeds the capacity of the vapor space.

In 1962, the American Petroleum Institute published API Bulletin 2518 which contained equations for estimating breathing losses and working losses from fixed roof tanks. These equations were used extensively by regulatory

TABLE 24. INPUT PARAMETERS REQUIRED FOR RECOMMENDED FIXED AND FLOATING ROOF MODELS

Parameter	Model A	Model B	Model C	Model D
M, molecular weight of vapor in storage tank	X	X	X	
P, true vapor pressure at bulk liquid conditions	X	X		
D, tank diameter	X		X	X
H, average vapor space height	X			
ΔT, average ambient diurnal temperature change	X			
F_P, paint factor	X			
C, adjustment factor for small diameter tanks	X			
K_C, product factor	X	X	X	
K_N, turnover factor		X		
K_S, seal factor			X	
V, average wind speed			X	
N, seal related wind speed exponent			X	
P^*, vapor pressure function			X	
E_F, secondary seal factor			X	
Q, average throughput				X
C, shell clingage factor				X
W_L, average organic liquid density				X

MODEL DESIGNATIONS

A. Fixed Roof Tank Breathing Losses (API-1962, modified by TRW/EPA).

$$L_B = 2.26 \times 10^{-2} M \left(\frac{P}{14.7-P}\right)^{0.68} D^{1.73} H^{0.51} \Delta T^{0.50} F_P CK_C$$

B. Fixed Roof Tank Working Losses (API-1962).

$$L_W = 2.40 \times 10^{-2} MPK_N K_C$$

C. External and Internal Floating Roof Tank Standing Storage Loss (API/EPA, 1980).

$$L_S = K_S V^N P^* DMK_C E_F$$

D. External and Internal Floating Roof Tank Withdrawal Loss.

$$L_W = \frac{(0.943)QCW_L}{D}$$

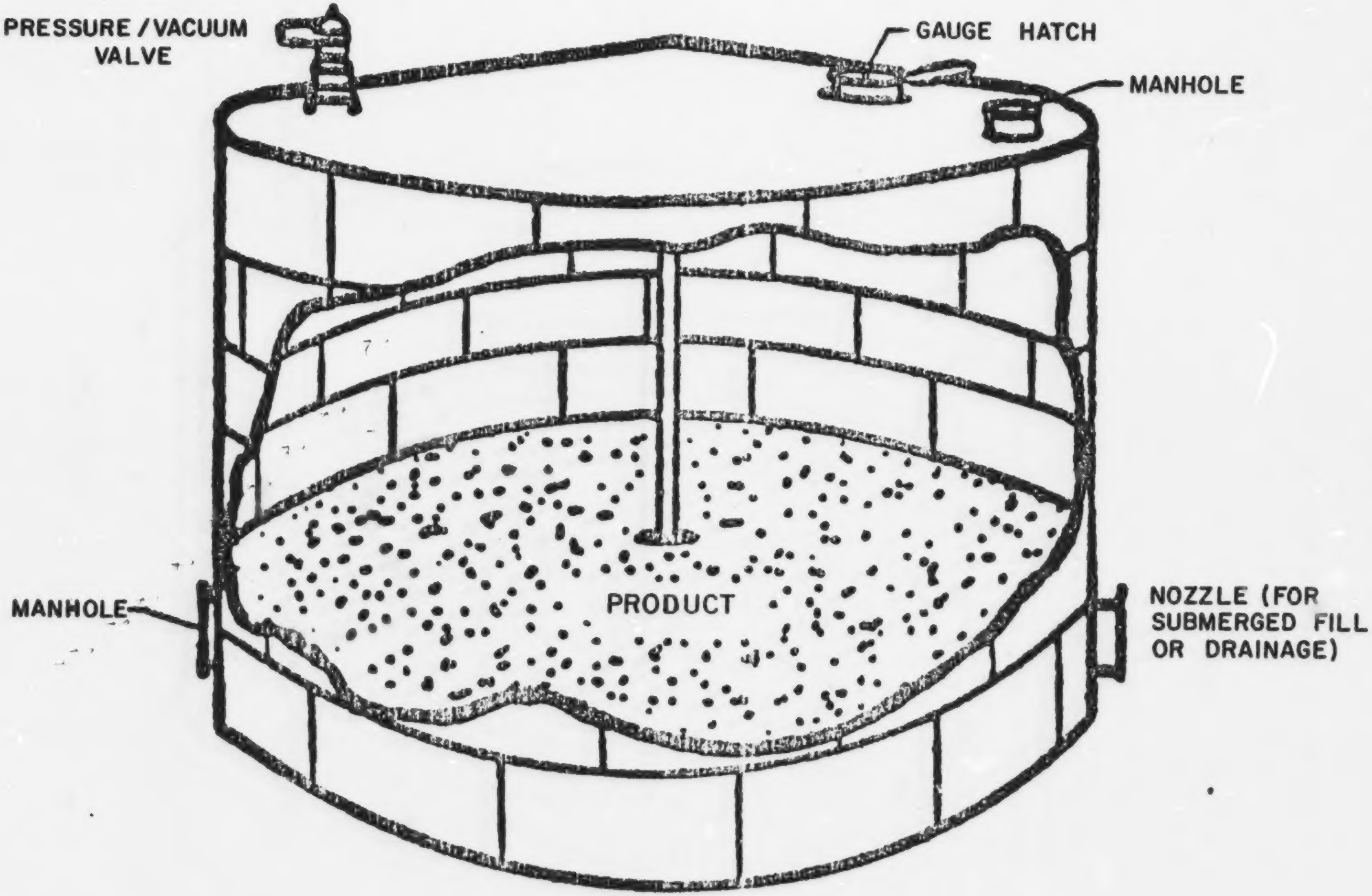
PRESSURE / VACUUM VALVE
GAUGE HATCH
MANHOLE
PRODUCT
MANHOLE
NOZZLE (FOR SUBMERGED FILL OR DRAINAGE)

Figure 7. Typical fixed roof storage tank (Masser - 1981).

agencies in the past to estimate air emissions from fixed roof tanks. However, test results reported by EPA (1979), the Western Oil and Gas Association (WOGA) (1977), and the German Society for Petroleum Science and Carbon Chemistry (DGMK), showed that the 1962 API equation for breathing losses over-estimated air emissions by roughly a factor of four. However, working losses estimated by the 1962 API equation were found to be fairly accurate.

Under EPA contract, TRW (1981), updated the breathing loss equation for fixed roof tanks based on the more recent test data. The revised equation provides breathing loss emission estimates which are 72 percent less than obtained by estimating emissions using the 1962 API equation. EPA's Office of Emission Standards Engineering Development (ESED) reported to GCA that the revised equation for breathing losses, prepared by TRW, and the 1962 API equation for working losses are the best available equations for fixed roof storage tanks. These equations are incorporated into a revised edition of EPA's emission factor handbook, AP-42 (April 1981). The revised AP-42 equations appear in Tables 25 and 26 for breathing and working losses, respectively, from fixed roof tanks.

The fixed roof working loss (L_W) is the sum of the loading and unloading losses. Special tank operating conditions may result in losses which are significantly greater or lower than the estimates provided by Table 23 and must be evaluated on a site-specific basis. The total losses from a fixed roof storage tank are equal to the sum of the breathing losses (L_B) and working losses (L_W).

Typical values for input parameters to the fixed roof tank equations appear in Tables 27 and 28, for breathing and working losses, respectively.

EXTERNAL AND INTERNAL FLOATING ROOF TANKS

External Floating Roof Tanks

Standing storage loss, the major element of evaporative loss, results from wind induced effects acting on the top of an external floating roof tank. The types of seals used to close the annular vapor space between the floating roof and the tank wall dictate the nature of wind effects. Figure 8 depicts a typical external floating roof storage tank.

Standing storage loss emissions from external floating roof tanks are controlled by either a primary seal, alone, or a primary and a secondary seal. Three basic types of primary seals used on external floating roofs are: (1) mechanical (metallic shoe); (2) resilient (nonmetallic); and (3) flexible wiper. Resilient seals are mounted to eliminate the vapor space between the seal and liquid surface (liquid mounted), or to allow a vapor space between the seal and liquid surface (vapor mounted). A primary seal closes the annular space between the edge of the floating roof and the tank wall. Some primary seals are protected by a metallic weather shield. Two configurations of secondary seals currently in use are: (1) shoe mounted; and (2) rim mounted. Although there are other seal system designs, Masser (1981) indicates that the systems described here comprise the majority in use today.

TABLE 25. RECOMMENDED MODEL FOR FIXED ROOF TANK BREATHING LOSSES (TRW UPDATE OF 1962 API MODEL)

$$L_B = 2.26 \times 10^{-2} M \left[\frac{P}{14.7-P}\right]^{0.68} D^{1.73} H^{0.51} \Delta T^{0.50} F_P C K_C$$

where:

L_B = fixed roof breathing loss (lb/year)

M = molecular weight of vapor in storage tank (lb/lb mole). See AP-42, Table 4.3-1.

P = true vapor pressure at bulk liquid conditions (psia). See note 1.

D = tank diameter (ft).

H = average vapor space height, including roof volume correction (ft). See Note 2.

ΔT = average ambient diurnal temperature change (°F).

F_P = paint factor (dimensionless). See AP-42, Table 4.3-2.

C = adjustment factor for small diameter tanks (dimensionless). See AP-42, Figure 4.3-4.

K_C = product factor (dimensionless). See Note 3.

Notes: (1) True vapor pressures for organic liquids can be determined from AP-42, Figures 4.3-5 or 4.3-6, or AP-42, Table 4.3-1.

(2) The vapor space in a cone roof is equal in volume to a cylinder which has the same base diameter as the cone and is one third the height of the cone.

(3) For crude oil, $K_C = 0.65$. For all other organic liquids, $K_C = 1.0$.

TABLE 26. RECOMMENDED MODEL FOR FIXED ROOF TANK WORKING LOSSES (1962 API MODEL)

$$L_W = 2.40 \times 10^{-2} MPK_NK_C$$

where:

L_W = fixed roof working loss (lb/10^3 gal throughput).

M = molecular weight of vapor in storage tank (lb/lb mole). See AP-42, Table 4.3-1.

P = true vapor pressure at bulk liquid conditions (psia). See Note 1.

K_N = turnover factor (dimensionless). See AP-42, Figure 4.3-7.

K_C = product factor (dimensionless). See Note 2.

Notes: (1) True vapor pressures for organic liquids can be determined from AP-42 Figures 4.3-5 or 4.3-6, or AP-42 Table 4.3-1.

(2) For crude oil, K_C=0.84. For all other organic liquids, K_C=1.0.

TABLE 27. TYPICAL RANGES OF INPUT PARAMETERS FOR FIXED ROOF TANK BREATHING LOSS MODEL:

$$L_B = 2.26 \times 10^{-2} M \left[\frac{P}{14.7-P}\right]^{0.68} D^{1.73} H^{0.51} \Delta T^{0.50} F_P C K_C$$

		Typical range of values	
Parameter symbol	Parameter description/units	For 95% of compounds	For 50% of compounds
M	Molecular weight of vapor in storage tank (lb/lb mole)	32-190	70-130[a]
P	True vapor pressure at bulk liquid conditions (psia)	0.00004-6.9@60°F[a]	1.0 - 4.0[a]
D	Tank diameter (feet)	14.7-98[b]	16-55[b]
H	Average vapor space height (ft)	7-33[b]	19-33[b]
T	Average ambient diurnal temperature change (°F)	±20° from average daily temp.[c]	±10° from average daily temp.[c]
F_P	Paint factor (dimensionless)	1.0-1.58[a]	1.2-1.4[a]
C	Adjustment factor for small diameter tanks	0.4-1.0[a]	0.7-1.0[a]
K_C	Product factor (dimensionless)	0.65-1.0[a]	0.65-1.0[a]

[a] Estimated from a review of data presented in AP-42.

[b] Estimated from a review of data presented in Erikson (1980).

[c] Engineering judgement.

TABLE 28. TYPICAL RANGES OF INPUT PARAMETERS FOR FIXED ROOF TANK WORKING LOSS MODEL:

$$L_W = 2.40 \times 10^{-2} MPK_NK_C$$

Parameter symbol	Parameter description/units	Typical range of values	
		For 95% of compounds	For 50% of compounds
M	Molecular weight of vapor in storage tank (lb/lb mole)	32-190[a]	70-130[a]
P	True vapor pressure at bulk liquid conditions (psia)	0.00004-6.9@60°F[a]	1.0-4.0[a]
K_N	Turnover factor (dimensionless)	0.22-1.0[a]	0.3-0.8[a]
K_C	Product factor (dimensionless)	0.84-1.0[b]	N.A.

[a] Estimated from a review of data presented in AP-42.

[b] K_C for crude oil = 0.84, K_C for all other organic liquids = 1.0. An average value of 0.95 is expected to be a good average value with high precision.

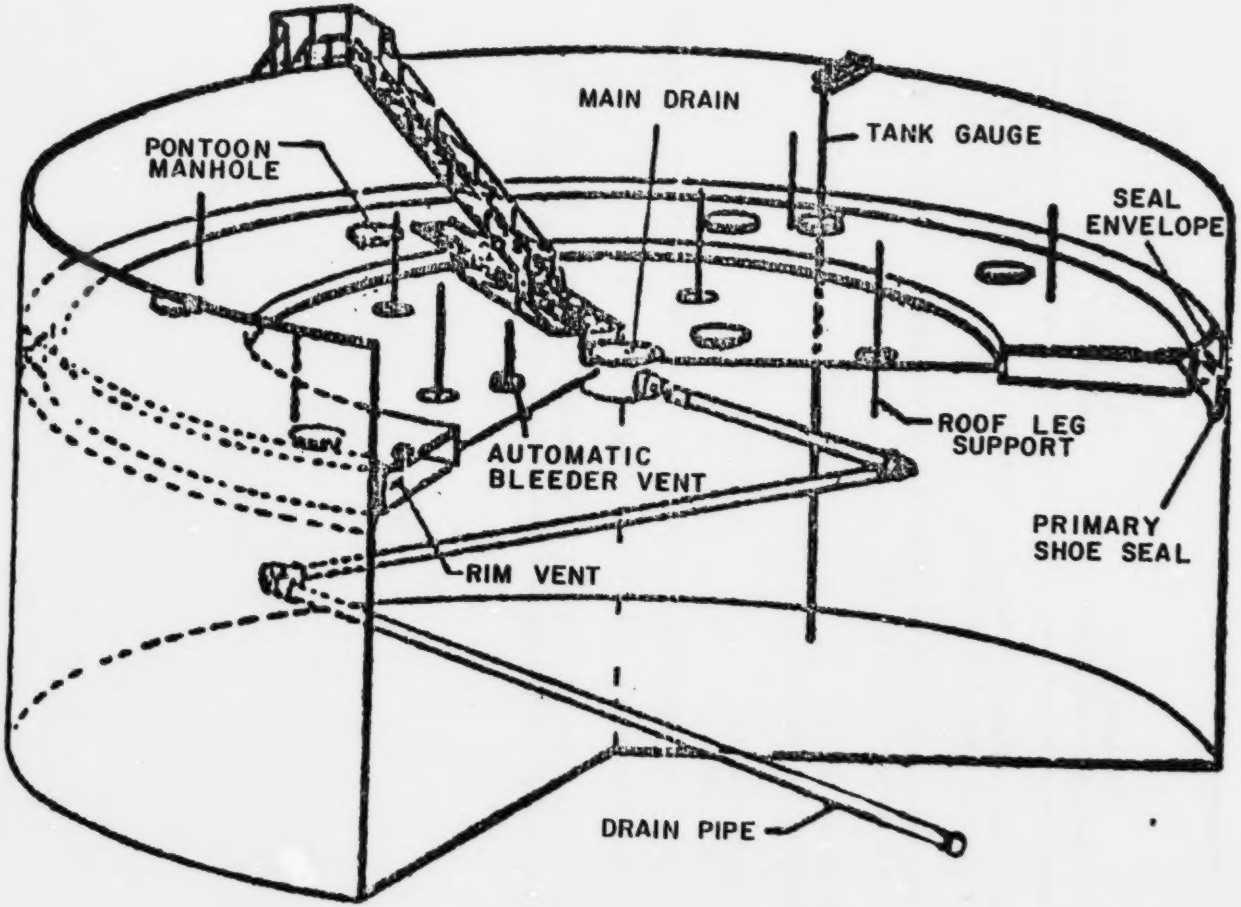
PONTOON MANHOLE
MAIN DRAIN
TANK GAUGE
SEAL ENVELOPE
ROOF LEG SUPPORT
AUTOMATIC BLEEDER VENT
PRIMARY SHOE SEAL
RIM VENT
DRAIN PIPE

Figure 8. Typical external floating roof storage tank (Masser - 1981).

Withdrawal loss is another source of emissions from external floating roof tanks. This loss is the vaporization of liquids that cling to the tank wall and are exposed to the atmosphere when a floating roof is lowered by withdrawal of liquid.

Internal Floating Roof Tanks

An internal floating roof storage tank has a permanently fixed roof and a cover inside the tank that either floats on the liquid surface (contact), or rests on pontoons several inches above the liquid (noncontact). Figures 9 and 10 illustrate the contact and noncontact design of internal floating roof storage tanks.

Internal floating roof tanks generally have the same sources of emissions as external floating roof tanks; i.e., standing storage and working losses. Fitting losses through deck fittings in the roof, roof column supports, or other openings, can also account for emissions from internal floating roof tanks.

Typical internal floating roofs incorporate two types of primary seals, resilient foam filled and wiper. Similar to those employed in external floating roof tanks, these seals close the annular vapor space between the edge of the floating roof and the tank wall.

Recommended Emission Estimation Techniques for Floating Roof Tanks

EPA's Office of ESED recommends in Supplement No. 12 to AP-42 the use of API's February 1980 Bulletin 2517, Evaporation Loss from External Floating Roof Tanks. According to McDonald (1982), EPA currently suggests two changes to the API equations presented in AP-42 for volatile organic liquid storage;

- Change the product factor, K_c, from 10 to 1;
- Disregard the secondary seal factor, E_F.

Based on the above changes, Table 29 shows EPA's currently recommended equation for standing storage losses from external floating roof tanks.

For estimating standing storage losses from internal floating roof tanks, EPA recommends the approach identified in API's June 1983 Bulletin 2519, Evaporation Loss from Internal Floating-Roof Tanks. Standing losses from internal floating roof tanks are derived by summing the losses estimated from the rim seal area, deck fittings, and deck seams.

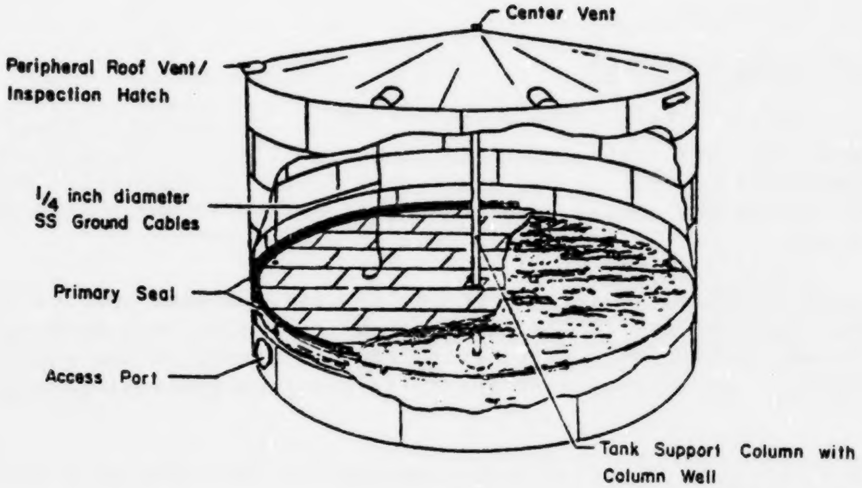
Center Vent
Peripheral Roof Vent/ Inspection Hatch
1/4 inch diameter SS Ground Cables
Primary Seal
Access Port
Tank Support Column with Column Well

Figure 9. Noncontact internal floating roof tank.

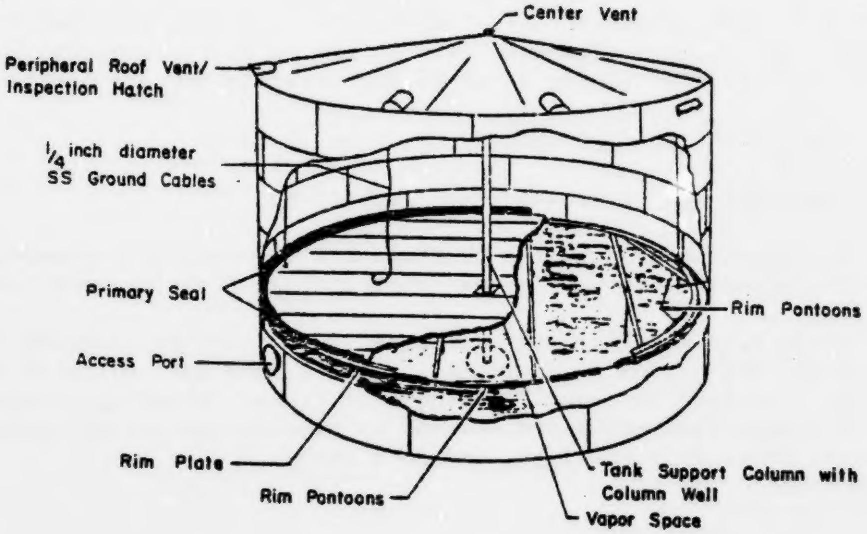
Center Vent
Peripheral Roof Vent/ Inspection Hatch
1/4 inch diameter SS Ground Cables
Primary Seal
Rim Pontoons
Access Port
Rim Plate
Rim Pontoons
Tank Support Column with Column Well
Vapor Space

Figure 10. Contact internal floating roof tank.

TABLE 29. EPA/API RECOMMENDED TECHNIQUE FOR STANDING STORAGE LOSSES FROM EXTERNAL FLOATING ROOF TANKS

$$L_S = K_S V^N P^* D M K_C$$

where: L_S = standing storage loss (lb/yr)

K_S = seal factor (lb-mole/(ft (mi/hr)^{N}yr)). See Note 1.

V = average wind speed at tank site (mi/hr). See Note 2.

N = seal related wind speed exponent (dimensionless). See Note 1.

P^* = vapor pressure function (dimensionless). See Note 3.

$$P^* = \frac{\left(\frac{P}{P_A}\right)}{\left[1 + \left(1 - \frac{P}{P_A}\right)^{0.5}\right]^2}$$

P = true vapor pressure at average actual organic liquid storage at temperature (psia)

P_A = average atmospheric pressure at tank location (psia)

D = tank diameter (ft)

M = average vapor molecular weight (lb/lb-mole). See Note 4.

K_C = product factor (dimensionless). See Note 5.

Notes: (1) For petroleum liquid storage: K_S and N for both primary only and primary/secondary seal systems are found in AP-42, Table 4.3-3.

(2) If the wind speed at the tank site is not available, wind speed data from the nearest local weather station may be used as an approximation.

(continued)

TABLE 29 (continued).

Notes (continued).

(3) P^* can be calculated or read directly from AP-42 Figure 4.3-8. True vapor pressures for organic liquids can be determined from AP-42 Figures 4.3-5 or 4.3-6, or AP-42 Table 4.3-1. If average actual organic liquid storage temperature, T_S, is unknown, the average storage temperature can be estimated from the average ambient temperature T_A(F) (available from local weather service data), adjusted by the tank paint color factor. See AP-42 Table 4.3-4.

(4) The molecular weight of the vapor, M, can be determined by AP-42 Table 4.3-1, analysis of vapor samples, or by calculation from the liquid composition. A typical value of 64 lb/lb-mole can be assumed for gasoline, and a value of 50 lb/lb-mole can be assumed for U.S. midcontinental crude oils.

(5) For all petroleum liquids except crude oil: $K_C = 1.0$

For crude oil: $K_C = 0.4$

For all volatile organic liquids: $K_C = 1.0$

Withdrawal losses from external floating roof tanks are determined by the EPA/API equation shown in Table 30. The total loss from floating roof tanks in lb/yr is estimated by the following equation:

$$L_T(\text{lb/yr}) = L_S(\text{lb/yr}) + L_W(\text{lb/yr}) \qquad (3)$$

where: L_T = total loss;

L_S = standing storage loss;

L_W = withdrawal loss.

The equation presented in Table 30 for external floating roof tanks was modified in API Publication 2519 for use in estimating withdrawal losses from internal floating roof tanks. The improvement in withdrawal loss estimate is obtained if the type and number of columns are known.

Tables 31 and 32 show typical ranges of values for input parameters to external floating roof model recommended by EPA.

OTHER STORAGE TANK MODELS

Several other models for storage tanks were found in GCA's literature search and through discussions with EPA and API. However, these approaches, as described below, are not considered state-of-the-art techniques.

Storage Tank Model Developed in the USSR

Moryakov, et al. (1979) presents a model developed in the USSR for estimating storage tanks emissions, but it appears to have two major drawbacks. First, the model is based on tests conducted in a northern climate and has not been thoroughly validated through field measurements. Moryakov reported that further experimental verification is required before the model can be used directly for southern climate zones.

The second major drawback is that the model does not account for what the authors termed small breathing losses. These losses are the equivalent of API's breathing losses for fixed roof tanks and standing storage losses for floating roof tanks. In the U.S., breathing losses are considered significant sources of emissions, and in some cases may exceed working losses or withdrawal losses.

In addition to the above drawbacks, the USSR model was developed to estimate emissions of petroleum products only. It is not known if the model is applicable for estimating emissions of volatile organic liquids.

TABLE 30. EPA/API RECOMMENDED TECHNIQUE FOR WITHDRAWAL LOSS FROM EXTERNAL FLOATING ROOF TANKS

$$L_W = \frac{(0.943)\ QCW_L}{D}$$

where: L_W = withdrawal loss (lb/yr).

Q = average throughput (barrel (bbl)/yr; 1 bbl = 42 U.S. gallons).

C = shell clingage factor (bbl/1000 ft^2). See AP-42, Table 4.3-5.

W_L = average organic liquid density (lb/gal). See Note 1.

D = tank diameter (ft).

Notes: (1) If W_L is not known, an average value of 6.1 lbs/gallon can be assumed for gasoline. An average value cannot be assumed for crude oil, since densities are highly variable.

(2) The constant, 0.943, has dimensions of (1000 $ft^3 \times gal/bbl^2$).

TABLE 31. TYPICAL RANGE OF INPUT PARAMETERS FOR WITHDRAWAL LOSS FROM EXTERNAL FLOATING ROOF STORAGE TANK MODEL:

$$L_W = \frac{(0.943)QCW_L}{D}$$

Parameter model	Parameter description/units	Typical range of values		Comments
		For 95% of compounds	For 50% of compounds	
Q	Average throughput (bbl/yr)	$6.0 \times 10^5 - 5.0 \times 10^4$	?	Average throughput varies greatly.
C	Shell clingage factor (bbl/1000 ft^2)	0.0015 - 0.6	0.0015 - 0.6	Clingage factor varies significantly dependent on the product stored and the shell condition.
W_L	Average organic liquid density (lb/gal)	N.A.	N.A.	An average value of 6.1 lb/gal can be assumed for gasoline. An average value cannot be assumed for crude oil or volatile organic liquids, since densities are highly variable (Masser - 1981).
D	Tank diameter (ft)	30 - 100	45 - 85	Variance between tank sizes is too great to select a constant.

[a] Based on a 40 m^3 tank turned over an average of 200 times per year and an 8,330 m^3 tank turned over an average 12 times per year. Average turnover rates obtained from Erickson (1980).

TABLE 32. TYPICAL RANGES OF INPUT PARAMETERS FOR EXTERNAL FLOATING ROOF TANK STANDING STORAGE LOSS MODEL:

$$L_S = K_S V^N P^* D M K_C$$

Parameter symbol	Parameter description/units	Typical range of values		Comments
		For 95% of compounds	For 50% of compounds	
K_S	Seal factor	0.2 - 1.2[a]	0.2 - 1.2[a]	The variance for K_S is great depending on the type of seal.
V	Average wind speed at tank site (mi/hr)	6.2 - 12.4[b]	7.2 - 10.6[b]	An average value of 8.9 has fairly high precision.
N	Seal related wind speed exponent (dimensionless)	0.4 - 2.6[b]	0.9 - 2.2[a]	The variance for N is great depending on the type of seal.
P*	Vapor pressure function (dimensionless)	0.05 - 0.7[b]	0.08 - 0.4[a]	The variance of P* is great depending on the true vapor pressure.
D	Tank diameter	30 - 100[c]	45 - 85[c]	Variance between tank sizes too great to select a constant.
M	Average vapor molecular weight (lb/lb-mole)	190 - 32[a]	130 - 70[a]	Variance too great between molecular weights of organic liquid vapors to select a constant.
K_C	Product factor	0.4 - 1.0[a]	0.4 - 1.0[a]	K_C = 0.4 for crude oil and 1.0 for all other organic liquids.

[a] Estimated from a review of data presented in AP-42.

[b] Estimated from a review of average wind speeds at 262 U.S. cities published by National Climate Center, Asheville, NC.

[c] Engineering estimate.

Outdated/Nonrecommended Models for Floating Roof Tanks

In 1962, API Bulletin 2517 presented equations for estimation standing storage loss and withdrawal loss for floating roof tanks. The equations did not differentiate between internal and external floating roof tanks. Input parameters for the API Bulletin 2517 equations appear in Table 33.

In 1978, the Chicago Bridge and Iron Company performed field measurements of emissions from a pilot test tank for EPA. Table 34 presents the equations developed from the pilot tests for both internal and open-top floating roof tanks equipped with primary seals alone, or both a primary and secondary seal. EPA's Office of ESED does not presently recommend use of these equations.

SPECIAL CONSIDERATIONS

Storage of Mixtures

The methods thus far reported for estimating storage tank air emissions are for pure compounds. However, to determine the air emission rate for a particular volatile component of a mixture, the emission factor equations presented are still applicable by using the true vapor pressure of the mixture instead of the pure compound vapor pressure.

The true vapor pressure of a mixture is the summation of partial pressures of each component in the stored liquid:

$$P_m^o = \sum P_i = \sum x_i \gamma_i P_i^o$$

where: P_m^o = vapor pressure of mixture;

P_i = partial pressure of component i;

x_i = mole fraction of component i in the liquid;

γ_i = activity coefficient of component i in the liquid;

P_i^o = vapor pressure of pure component i.

The activity coefficient corrects for deviations from Raoult's Law to account for liquid interactions. For hydrocarbon mixtures, it is generally assumed that Raoult's Law holds, thus the activity coefficient is taken as unity. This activity coefficient is a function of mixture composition and relative concentration. Although the activity coefficients for a particular mixture can be determined experimentally, empirical correlations are provided by Lyman, et al. (1982).

It should be noted that by using the vapor pressure of the mixture in the storage tank models, the emissions estimate will be as total volatile organic carbon (VOC). The concentration of component i in the vapor phase is the

TABLE 33. INPUT DATA FOR 1962 API FLOATING ROOF MODEL

Standing storage loss	Withdrawal loss
Molecular weight of vapor in storage tank	Density of stored liquid
True vapor pressure at bulk conditions	Tank construction factor
Tank diameter	Tank diameter
Average wind velocity	
Tank type factor	
Seal factor	
Paint factor	
Crude oil factor	

TABLE 34. FLOATING ROOF EQUATIONS BASED ON 1978 PILOT TESTS (NOT RECOMMENDED FOR USE)

$$L_T = L_{WD} + L_S + L_F$$

$$L_S = K_S \; V^n \; M \; D \quad \frac{\frac{P}{(14.7)}}{\left[1 + (1 - \frac{P}{14.7})^{0.5}\right]^2} \quad \frac{1}{2205}$$

$$L_F = NK_F \; V^n \; M \quad \frac{\frac{P}{(14.7)}}{\left[1 + (1 - \frac{P}{14.7})^{0.5}\right]^2} \quad \frac{1}{2205}$$

$$L_{WD} = 0.000198DTHd \; 1/2205$$

where: L_T = total loss (mg/yr);

L_{WD} = withdrawal loss (mg/yr);

L_S = seal loss (mg/yr);

L_F = fitting loss (mg/yr);

M = molecular weight of product vapor (lb/lb-mole); 78.1 lb/lb-mole for VOC;

P = true vapor pressure of product (psia); 2 psia assumed;

D = tank diameter (ft);

V = average wind speed for the tank site (mph); 10 mph assumed average wind speed;

K_s = seal factor

K_F = fitting factor

n = seal wind speed exponent

m = fitting wind speed exponent

C = product withdrawal shell clingage factor

N = fitting multiplier

T = turnovers (per yr),

H = tank height (ft),

d = density of stored liquid at bulk liquid conditions (lb/gal; use 8.0).

partial pressure of component i (P_i) divided by the vapor pressure of the mixture (P^o_m). Thus, the emission rate contribution for component i is determined by multiplying the calculated emission rate for the mixture by the vapor phase mole fraction of component i.

Open Storage Tanks

Generally, it is unusual to find pure volatile organic liquids stored in open tanks. However, it may be possible that certain wastes such as sludges are stored in open tanks prior to treatment or disposal. The mechanisms of molecular and turbulent diffusion will control the process of evaporation. Thus, the methods for determining an emission rate for this type of storage becomes similar to that developed for surface impoundments.

The major difference between a surface impoundment and an open storage tanks is the potential for a greater freeboard effect. For a substantial freeboard (i.e., greater than the fetch), the wind effect on the liquid surface becomes negligible, thus the emission rate controlling step becomes the molecular diffusion of component i in the waste sludge.

SECTION 8

AIR EMISSION ESTIMATION TECHNIQUES FOR WASTEWATER TREATMENT PROCESSES

INTRODUCTION

The purpose of this section is to identify AERR models which can be used for quantifying air emissions of volatile compounds from hazardous waste treatment systems. The approach used for identifying the appropriate AERR model was to categorize each treatment system into one of these main categories:

- open tanks with no mixing;
- open tanks with mixing; and
- closed systems.

In the case where all volatile species in the waste stream have been identified, and their effluent concentrations measured, AERR models for aerated or nonaerated surface impoundments could be applied to open tank processes depending upon system dynamics (i.e., aerated or nonaerated). For closed system wastewater treatment processes, it can be assumed that aside from system leakage or operational abnormalities, there are no air emissions. The concentration of effluent contaminants can be calculated based on process unit efficiency. Such calculations are provided in the literature but will not be discussed in this report.

Limited data are available regarding the removal efficiency and effluent concentrations for organic pollutants subjected to various biological treatment systems. If outlet concentrations are not available for the subject facility, these limited data may provide a rough cut estimate of the in-tank concentration for a specific compound. However, caution is advised since it is likely such data were developed for single component waste streams. Interactions of multicomponent waste streams will affect the system removal efficiency.

Emissions estimation techniques have been developed for biological treatment processes when only inlet concentrations are known. These models take into consideration pollutant removal by degradation, adsorption and air stripping. A formal discussion of each model is provided in this section.

OPEN TANK SYSTEM-NO MIXING

Typical wastewater treatment systems that fall into the category of open tank-no mixing are:

- sedimentation;
- chlorination;
- equalization.

No AERR Models were located that specifically described air emissions from these treatment systems. However, it can be assumed that these systems fall into a broader category of nonaerated surface impoundments. Treatment systems that fall into the open tank-no mixing category represent plug flow systems. Therefore, applying the nonaerated surface impoundment model one needs to accurately define the in-tank concentration of the specific compound in question.

As described in Section 4, Mackay and Leinonen (1975) presented a surface impoundment model for plug flow, where the in-tank concentration was defined by:

$$C_i = C_{io} \exp(-K_{iL}\, t/L)$$

where:

C_i = concentration of compound i at time t (mol/m^3);

C_{io} = initial concentration of compound i (mol/m^3);

K_{iL} = overall liquid phase mass transfer coefficient (m/hr);

t = residence time (hr);

L = impoundment depth (m).

This is a simple, first-order decay method for calculating the in-tank concentration, however, the term K_{iL} only accounts for a compound's loss by volatilization. A more correct application would be to define the effects of sorption and probably chemical conversion.

OPEN TANK-MIXING: BIOLOGICAL TREATMENT SYSTEMS

GCA's evaluation of open tank treatment processes with mixing focused mainly on the activated sludge biological treatment process (high rate mixing). Other processes, which might fall into the low rate mixing subcategory, include neutralization or precipitation involving the addition and rapid mixing of a chemical reagent. The emissions from these processes are best described by application of Thibodeaux's Aerated Surface Impoundment (ASI) model using very low power input to identify the area of turbulent mixing. This model was previously discussed in detail in Section 4.

Major research and development efforts of models to predict hazardous chemical air emissions from biological treatment processes have been conducted by Hwang and Freeman. The following discussion of AERR models developed by these two researchers identifies basic similarities in approach and differences in model details. In addition, Thibodeaux's ASI model is discussed in the context to which it can be applied to the activated sludge (AS) biological treatment process. In summary, four basic models to predict air emissions release rates from the AS process are discussed as follows:

- Thibodeaux (1981d)--ASI model;
- Hwang (1980)--activated sludge surface aeration (ASSA) model;
- Freeman (1979)--ASSA model;
- Freeman (1980)--diffused air activated sludge (DAAS) model.

Table 35 summarizes input parameters required for each model reviewed by GCA. The following sections discuss these models in detail.

All of the models presented predict the air emissions rate based on the concentration of compound i in the aeration basin of the activated sludge (AS) process. For a well mixed system, the basin concentration of a specific compound is assumed equal to the effluent concentration. Models which predict emissions based on the influent concentration (S_o or C_i) of the compound tend to be very complex compared to models which assume a known effluent concentration (S_e). Three of the four models reviewed can be applied to surface aeration AS systems, whereas only the Freeman DAAS is directly applicable to diffused air systems. In general, the Hwang ASSA model tends to be both adequate and simple to apply compared to Freeman's model.

Hwang (1980) Activated Sludge Surface Aeration

Hwang's Activated Sludge (AS) treatment AERR model employs techniques presented earlier for predicting emissions from aerated surface impoundments under steady state conditions (Thibodeaux, Parker, and Heck, 1981). The model by Thibodeaux et al., predicts the air emission rate of a compound based on the concentration of the compound (substrate concentration, S_e) within the impoundment. Hwang notes that for AS treatment systems, AERR models should consider removal of the compound by: (1) biological oxidation; (2) air stripping; and (3) adsorption to wasted sludge. Thus, Hwang's model predicts the effluent concentrations that result when the mass balance for the compound across the AS process is satisfied. The emission rate from the process is then predicted by the aerated surface impoundment equation. Note that if the pollutant's effluent concentration for an AS process is known, the emission release rate for that pollutant can be calculated directly by the aerated surface impoundment equation. This is based on the complete mix assumption that the effluent concentration adequately represents the concentration of the compound in the aeration tank.

TABLE 35. SIMPLIFIED LIST OF INPUT PARAMETERS REQUIRED FOR EACH ACTIVATED SLUDGE BIOLOGICAL TREATMENT MODEL[a]

Parameter	Thibodeaux (1981d)[b] ASI model	Hwang (1980)[c] ASSA model	Freeman (1979)[d] ASSA model	Freeman (1980)[e] diffused air mass transfer model
Air emission rate of hazardous substance i	Q_i	Q_i	N_a	
Overall mass transfer coefficient	K_L	K_a	K_L	K_1
Total surface area of basin	A_s	A_s	A_s	
Mole fraction of compound i in the liquid	X_i	X_i	X_i	X_i
Mole fraction of compound i at equilibrium	X_i^*	X_i^*	X_i^*	X_i^*
Molecular weight of compound i	MW_i	MW_i	MW_i	MW_i
Effluent concentration of compound i		S_e	C_o	
Influent concentration of compound i		S_o	C_I	
Recycle ratio, flow rate recycle/flow rate feed		r		
Hydraulic residence time		t_c		
Concentration of micro-organisms in basin		X	B_O	
Grau's Biokinetic rate constant		$k_{i(s)}$		
Concentration of total substrates		S_T		
Ratio waste sludge flow/feed flow		W		
Concentration of substrate (compound i in recycle)		S_r	C_R	
Adsorption constants		K_1, K_T		
Maximum concentration of substrate on sludge		X'		
Stripping rate constant		k_a		
Concentration of micro-organisms in recycle			B_R	
Concentration of micro-organisms in influent			B_i	
Concentration of oxygen in influent			O_I	
Concentration of oxygen in effluent (basin)			O_O	
Concentration of oxygen in recycle			O_R	
Feed flow rate			F_I	
Effluent flow rate			F_O	
Recycle flow rate			F_R	
Diameter of region of effect for mass transfer in the turbulent zone			D	

(continued)

TABLE 35 (continued)

Parameter	Thibodeaux (1981d)[b] ASI model	Hwang (1980)[c] ASSA model	Freeman (1979)[d] ASSA model	Freeman (1980)[e] diffused air mass transfer model
Mass transfer coefficient for organic compound i turbulent zone, convective zone			K_a^T, K_a^C	
Mass transfer coefficient for oxygen turbulent zone, convective zone			K_b^T, K_b^C	
Gerber's biokinetic rate constants			K_s, K_{O_2}, K_1, K_2, K_3	
Number of aerators in basin			N	
Oxygen transferred to basin			N_{O_2}	
Rate of organic disappearance			r_a	
Rate of micro-organism growth			r_b	
Rate of oxygen use			r_{O_2}	
Substrate use factor, lb mole micro-organism produced/lb mole substrate consumed			s	
Oxygen use factor, lb mole micro-organism produced/lb mole oxygen consumed			t	
Basin volume			v	
Interfacial area per unit volume of basin				a_v
Effective mean bubble diameter				D_B
Diffusivity of compound i in water				D_{i,H_2O}
Acceleration of gravity				g
Overall mass transfer coefficient to bubble from liquid				K_x
Molecular weight of air				MW_{air}
Molecular weight of water				MW_{H_2O}
Distribution coefficient, $m_i = \frac{y_i}{X_i}$				m_i
Power input to liquid per unit volume of basin				(P/V)
Liquid phase Schmidt number = $\frac{\mu_l}{\rho_l D_{i,H_2O}}$				Sc
Volume of bubble				V_B
Superficial gas velocity				V_G

(continued)

TABLE 35 (continued)

Parameter	Thibodeaux (1981d)[b] ASI model	Hwang (1980)[c] ASSA model	Freeman (1979)[d] ASSA model	Freeman (1980)[e] diffused air mass transfer model
Superficial liquid velocity				v_l
Rise velocity of a bubble swarm				v_s
Terminal velocity of a single rising bubble				v_t
Mole fractions of compound in gas				y
Mole fraction of compound in gas as it enters bottom of basin				y_1
Mole fraction of compound in gas as it breaks the surface of the basin				y_2
Total rise time of bubble in basin, hours				θ
Viscosity of liquid				μ_l
Density of gas				ρ_g
Density of liquid				ρ_l
Surface tension of liquid				σ
Time				τ
Gas holdup fraction in basin				ψ

[a] Parameters used in computing mass transfer coefficients not included (See Section 4 for details)

[b] Thibodeaux (1981d) ASI model $Q_i = K_L A_s (X_i - X_i^*) MW_i$

[c] Hwang (1980) ASSA model

(1) without adsorption to sludge

$$S_e = \frac{S_o}{1 + \frac{k_{1(s)}X}{S_o}(1+r)t_c + (1+r)k_a t_c}$$

(2) with adsorption to sludge

$$S_e = \frac{-b + \sqrt{b^2 + 4\ a\ S_o(1+K_T S_r)}}{2\ a}$$

where

$$b = 1 - K_l S_o + K_T S_r + \frac{k_{1(s)}X}{S_o}(1+r)t_c(1+K_T S_r) + k_a(1+r)t_c(1+K_T S_r) + K_l\ X'\ (1+r)W$$

$$a = K_l\ (1 + (1+r)\frac{k_{1(s)}X}{S_o}t_c + (1+r)\ k_a t_c)$$

(continued)

TABLE 35 (continued)

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[d] Freeman (1979) ASSA model

(1) For substance balance

$$C_I F_I + F_r C_r = C_0 F_0 + \overbrace{\left| N \frac{\pi D^2}{4} K_a^T (X_a) + \left(A_S - \frac{N D^2}{4}\right) K_a^c X_a \right|}^{N_a} MW_a + \overbrace{\left| \frac{t}{s} \left(\frac{K_5 B_0 C_0 O_0}{\frac{k_5}{k_1} O_0 + K_{O_2} K_S + C_0 O_0 + K_{O_2} C_0} \right) \left(\frac{MW_a}{MW_{O_2}} \right) \right|}^{r_a} V$$

$$\text{where} \quad X_a = C_0 \left(\frac{MW_{H_2O}}{MW_a} \right) \frac{1}{\rho_{H_2O}}$$

(2) For micro-organism balance

$$B_I F_I + F_r B_r = B_0 F_0 - \overbrace{\left| t \left(\frac{k_5 B_0 C_0 O_0}{\frac{k_5}{k_1} O_0 + K_{O_2} K_S + C_0 O_0 + K_{O_2} C_0} \right) \frac{MW_B}{MW_{O_2}} \right|}^{r_b} V$$

(3) For oxygen balance

$$O_I F_I + F_r O_r = O_0 F_0 + \overbrace{\left(\frac{k_5 B_0 C_0 O_0}{\frac{k_5}{k_1} O_0 + K_{O_2} K_S + C_0 O_0 + K_{O_2} C_0} \right)}^{r_{O_2}} V - \overbrace{\left[N \frac{\pi D^2}{4} K_b{}^T \left(X^*_{O_2} - X_{O_2} \right) + \left(A_s - \frac{N D^2}{4} K_b{}^c \right) \left(X^*_{O_2} - X_{O_2} \right) \right]}^{N_{O_2}} MW_{O_2}$$

$$\text{where} \quad X_{O_2} = O_0 \left(\frac{MW_{H_2O}}{MW_{O_2}} \right) \frac{1}{\rho_{H_2O}}$$

[e] Freeman (1980) DAAS model mass transfer equations

$$y_2 = m X_1 \left| 1 - \mathrm{EXP} \left(\frac{-6 K_x \theta MW_{air}}{D_B \rho_g m} \right) \right| + y_1 \mathrm{EXP} \left(\frac{-6 K_x MW_{air}}{D_B \rho_g m} \right)$$

$$\text{where:} \quad D_B = 4.15 \left(\frac{\sigma^{0.6}}{(P/V)^{0.4} \rho_1^{0.2}} \right) \psi^{1/2} + 0.09 \text{ cm}$$

$$(P/V) = V_G \rho_1 g + V_1 \rho_1 g$$

$$V_S = 27.43 \text{ cm/sec} + 2 V_G$$

$$\Psi = \frac{V_G}{0.9 \text{ ft/sec} + 2 V_G}$$

$$a_v = 1.44 \left| \frac{(P/V)^{0.4} \rho_1^{0.2}}{\sigma^{0.6}} \right| \left(\frac{V_G}{V_t} \right)^{1/2}$$

$$k_1 (Sc)^{1/2} = 0.42 \left| \frac{(\rho_1 - \rho_g) \mu_1 g}{\rho_1^2} \right|^{1/3} (3600) \frac{1}{MW_{H_2O}}$$

Figure 11 presents a schematic of the continuous AS process and defines the terms used by Hwang and others. Hwang describes the dynamics of substrate removal in the AS process by employing the following material balance:

$$\begin{matrix}\text{Input in} \\ \text{Influent}\end{matrix} - \left[\underbrace{\begin{matrix}\text{(1)} \\ \text{Biodegradation}\end{matrix} + \begin{matrix}\text{(2) Air} \\ \text{stripping}\end{matrix} + \begin{matrix}\text{(3) Sludge} \\ \text{wastage}\end{matrix}}_{}\!\!\!\!\overset{\text{Removal by:}}{}\right] = \begin{matrix}\text{Output in} \\ \text{Effluent}\end{matrix}$$

$$Q_F S_o - \left[\frac{K_{1(s)} X S_e}{S_o} V + (K_a S_e V) + Q_w \frac{K_1 X' S_e}{1 + K_T S_r + K_1 S_e}\right] = (Q_F - Q_w) S_e$$

where:

X = sludge concentration in reactor (µg/l);

X' = maximum concentration of substrate on sludge (µg/l);

$K_{1(s)}$ = Grau equation rate constant, n=1 (1/day).

Upon simplification and rearrangement;

$$(S_o - S_e) = \left[\frac{K_{1(s)} X S_e}{S_o}\right](1+r)\, t_c + K_a (1+r)\, S_e\, t_c + W(1+r)\left[\frac{K_1 X' S_e}{1 + K_T S_r + K_1 S_e}\right]$$

Further rearrangement of the above equation yields the two solution methods presented in Table 36. The first method presented in Table 36 predicts air emissions from the AS process by requiring the solution of a quadratic equation in order to obtain S_e. The second solution method is based on the assumption that adsorption to the waste sludge is negligible which is true in many instances.

Biodegradation Kinetics--

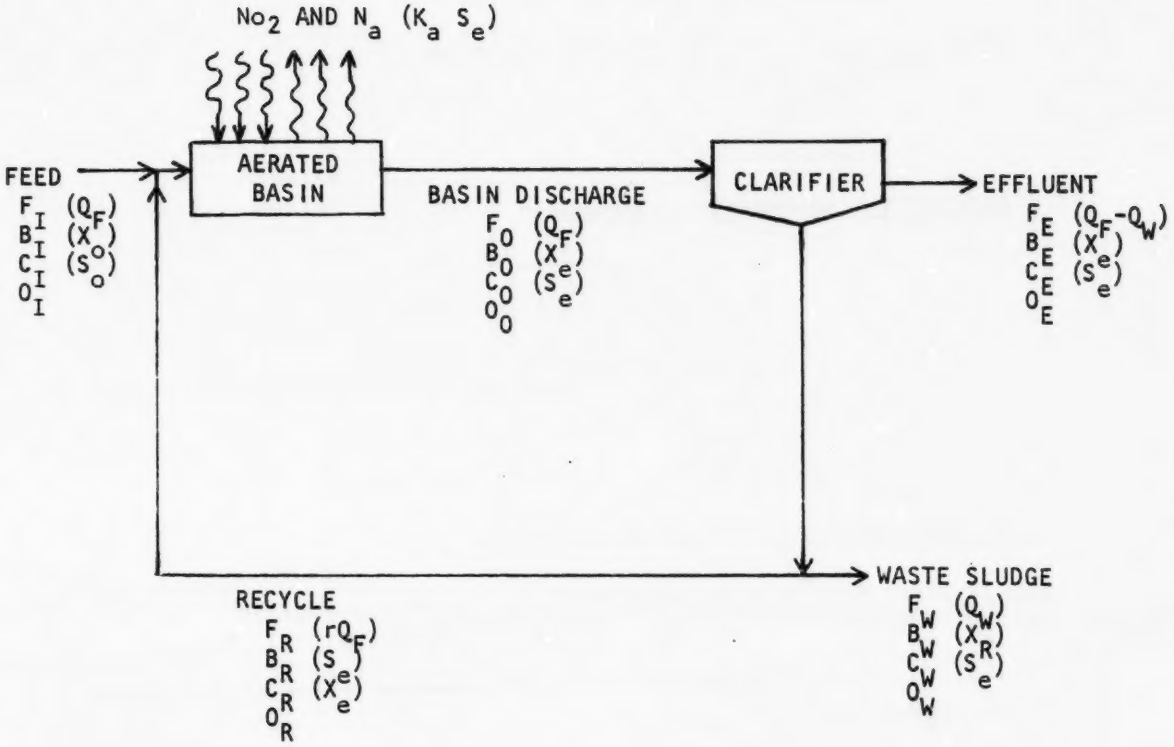
Hwang evaluated the four biodegradation kinetic models listed below with respect to the AS process:

1. First order kinetics: $-\frac{dS}{dt} = k_1 X S$

2. Monod (1942) kinetics: $-\frac{dS}{dt} = \frac{\hat{u} X}{Y} \frac{S}{k_s + S}$

3. Grau (1975) kinetics: $-\frac{dS}{dt} = k_{n(s)} X \left(\frac{S}{S_o}\right)^n$; where n = 1

4. Hwang (1980) kinetics: $-\frac{dS}{dt} = \frac{k_3 X S}{(1 + k_4 S) S_o}$


No_2 AND N_a (K_a S_e)
AERATED BASIN
CLARIFIER
FEED
F_I (Q_F)
B_I (X_o)
C_I (S_o)
O_I
BASIN DISCHARGE
F_O (Q_F)
B_O (X_e)
C_O (S_e)
O_O
EFFLUENT
F_E (Q_F-Q_W)
B_E (X_e)
C_E (S_e)
O_E
RECYCLE
F_R (rQ_F)
B_R (S)
C_R (X_e)
O_R
WASTE SLUDGE
F_W (Q_W)
B_W (X_R)
C_W (S_e)
O_W

NOTE: FREEMAN'S NOTATION F_I, B_I, C_I, O_I, ETC., WITH THE CORRESPONDING HWANG'S NOTATION IN PARENTHESES.

Figure 11. Model of activated sludge system.

TABLE 36. HWANG (1980) ACTIVATED SLUDGE TREATMENT PROCESS AERR MODEL

Model Form:[a]

$$Q_i = 4047 \times 10^4 \; MW_i \; K_{Li} \; \bar{A} \; x_i$$

where $x_i = (Se) \; MW_{H_2O}/10^6 \; MW_i$

$$K_{Li} = (K_{Li})_c \frac{\bar{A}_c}{\bar{A}} + (K_{Li})_T \frac{\bar{A}_T}{\bar{A}}$$

for significant absorption to waste sludge:

$$S_e = \frac{- b + \sqrt{b^2 + 4 \; a \; S_o(1 + K_T S_r)}}{2 \; a}$$

where $b = 1 - K_1 S_o + K_T S_r + \frac{k_{1(s)} X}{S_o} (1+r) t_c (1+K_T S_r) + k_a (1+r) t_c (1+K_T S_r) + K_1 \; X' \; (1+r) \; W$

$$a = K_1 \; (1 + (1+r) \frac{k_{1(s)} X}{S_o} t_c + (1+r) \; k_a \; t_c)$$

excluding adsorption to waste sludge (X' small):

$$S_e = \frac{S_o}{1 + \frac{k_{1(s)} X}{S_o} (1+r) \; t_c + (1+r) k_a \; t_c}$$

[a]Definitions:

Q_i = emission rate of chemical i (g/s)

MW_i = molecular weight of chemical i (g/g mole)

K_{Li} = overall mass transfer coefficient of chemical i expressed in liquid phase concentration ($gmol/cm^2 - s$)

$\bar{A}_c$ = surface area of the impoundment expressed in acres (Subscript c denotes the convective area of the surface impoundment; subscript T denotes the turbulent area)

x_i = mole fraction of component i in the liquid phase

4047×10^4 = denotes the factor needed to convert the surface area expressed in acres to cm^2

X = sludge concentration in reactor (μg/l)

X' = maximum concentration of substrate (compound i) on sludge (μg/l)

$k_{1(s)}$ = Grau equation rate constant n=1 (1/day)

S_o = initial substrate concentration (μg/l)

k_a = area averaged overall air stripping rate constant (1/day)
Note: K_{Li} may be converted to k_a as described earlier under surface impoundments

The suitability of each biokinetic model was tested by Hwang with data from the following sources:

- EPA, Cincinnati, Ohio; Batch experiments using over 50 pure priority pollutants at initial concentrations of 5 and 10 mg/L.
- Union Carbide Corporation; Continuous flow reactors, two in series, for BOD degradation of wastewater.
- Catalytic, Inc.; Continuous flow reactor using synthetic mixtures of pure components; BOD analyzed.
- J. WPCF; Continuous flow reactor for biodegradation of benzidine in wastewater.

Hwang noted that increased initial concentrations resulted in decreased removal efficiencies, thus eliminating the first order kinetics model from consideration. Grau kinetics and Hwang kinetics proved superior to Monod or first order kinetics in fitting the data. The difference between the Grau and Hwang kinetics was determining whether the plot of $Xt/S_o\ (S_o-S_e)$ versus $1/S_e$ yields a straight line through the origin of the plot. Hwang found that in most cases the Grau kinetics model (n=1) adequately described biodegration kinetics. Thus, the rate of organic (substrate) removal is expressed as:

$$-\frac{dS}{dt} = \frac{k_{1(s)}\ X\ S}{S_o}$$

where:

dS/dt = rate of substrate removal (μg/l/day);

X = biomass concentration (ppm);

S = substrate concentration (usually S_e) (μg/l);

S_o = initial substrate concentration (μg/l);

$k_{1(s)}$ = Grau kinetics rate constant (n=1) (1/day).

Determination of Biokinetics Rate Constants--

In order to apply the above biokinetics model to an AS system one must know the Grau kinetics rate constant $k_{1(s)}$ specific to the substrate compound of concern. Determination of the biokinetic rate constant $k_{1(s)}$ can be accomplished by fitting laboratory or field data to the Grau kinetics material balance;

$$\frac{Xt}{S_o\ (S_o-S_e)} = \left|\frac{1}{k_{1(s)}}\right| \frac{1}{S_e}$$

Plotting $Xt/S_o\,(S_o-S_e)$ versus $1/S_e$, should yield a straight line through the origin at a slope of $1/k_{1(s)}$. Hwang has developed values for Grau's $k_{1(s)}$ for most of the 129 priority pollutants based on; (1) laboratory and field data cited above; and (2) estimates based on observed similarities between compounds extended to include untested compounds.

Air Stripping Kinetics--

The expression for air stripping of volatile compounds (substrate) from the AS treatment basin is given as:

$$-\frac{dS}{dt} = k_a\,S$$

(for single component substrate system)

where:

k_a = air stripping rate constant, 1/day.

Hwang employs the area-averaged mass transfer model used by Thibodeaux (1981d), where the overall mass transfer coefficient k_a is based on the area-averaged k-values for zones of turbulence $(k_a)_T$ and convection $(k_a)_c$ as shown below:

$$k_a = (k_a)_T\,\frac{A_T}{A} + (k_a)_c\,\frac{A_c}{A}.$$

Key assumptions of this model are that the AS system can be approximated as two distinct zones where mass transfer takes place at the surface of the reactor only and is only slightly influenced by subsurface phenomena.

Discussions presented earlier on methods for calculating turbulent and convective zone mass transfer coefficients for use in the above expression are applicable here and will not be repeated. Note that in many cases mass transfer is liquid phase controlled, but, for some low volatility compounds the gas phase mass transfer may be equally controlling. In many cases the turbulent zone will be the major contributor of volatile air emissions, however, Hwang notes that for large lagoons with poor aeration this may not be so.

Adsorption on Sludge--

Hwang contends that adsorption onto waste activated sludge may be a significant removal mechanism for some organic priority pollutants and cyanides. Hwang assumes a Langmuir type adsorption equation to describe the equilibrium concentration of the substrate (for a single component system) on the sludge as:

$$[B.S] = \frac{K_1\,X'\,S}{1 + K_1\,S + K_T\,S_r}$$

where:

[B.S] = concentration of a substrate on sludge, μg/l;

S = substrate concentration in the liquid, μg/l;

S_r = concentration of total substrates minus substrate S under consideration, μg/l;

K_1, K_T = adsorption constants;

X' = the maximum amount of the substrate adsorbed on sludge, μg/l.

Similarly, for a multicomponent substrate system the above equation becomes:

$$[B.S_T] = \frac{K_T\ S_T\ X'_T}{1 + K_T\ S_T}$$

(for multicomponent substrate system).

Note that the AS treatment system AERR model presented in Table 36 includes the sludge adsorption term for single component systems.

Kincannon et al. (1981,1982) investigated the importance of each pollutant mechanism (air stripping, sorption and biodegradation) from lab-scale activated sludge treatment systems and found that sorption was not an important mechanism for any of the priority pollutants analyzed. Although some exceptions applied, the most predominate removal mechanism was found to be consistent with chemical classification. For instance, biodegradation removal was predominate for nitrogen compounds, phenols and oxygenated compounds. Aromatics were removed from wastewater by a combination of biodegradation and air stripping, while halogenated hydrocarbons were removed by air stripping.

Determination of Adsorption Rate Constants--

Hwang also presents a method for determining the adsorption rate constants. The above two equations can be rearranged and linearized as follows:

$$\frac{1}{[B.S]} = \frac{1 + K_T\ S_r}{K_1\ X'}\left(\frac{1}{S_e}\right) + \frac{1}{X'}$$

(single component).

$$[B.S] = \frac{1}{K_T\ X_T}\ \frac{1}{S_T} + \frac{1}{X'_T}$$

(multicomponent).

The values of K_T and X_T' are determined by plotting $1/[B.S_T]$ versus $1/S_T$ for single component substrates. Similarly, a plot of $1/[B.S]$ versus $1/S_e$ can be prepared for multicomponent substrate systems. Data presented by Hwang may be used to develop these rate constants. In addition, Hwang has provided a listing of these rate constants for the priority pollutants based on work sponsored by EPA.

Freeman (1979) Activated Sludge Surface Aeration Model

Freeman's original AS treatment AERR model appears very similar to the work of Thibodeaux (1981d) and Hwang (1980). The major difference between the Freeman and Hwang AS models are the biodegradation kinetics used. In addition, Freeman does not address adsorption of substrate onto the wasted sludge, assuming that adsorption is not a major removal mechanism for organic pollutants. This is a reasonable assumption based on the most recent work of Kincannon mentioned previously.

Freeman uses Thibodeaux's aerated surface impoundment AERR model, based on the two-film resistance theory, to predict the emissions from the AS basin knowing the concentration of substrate in the basin. However, in order to predict the concentration of substrate, Freeman writes the material balance around the basin for the substrate, C, the micro-organisms, B, and oxygen, O, as follows:

$$C_I F_I + F_R C_R = C_O F_O + N_a + r_a V \quad \text{(for compound A)}$$

$$B_I F_I + F_R B_R = B_O F_O - r_b V \quad \text{(for biomass B)}$$

$$O_I F_I + F_R B_R = O_O F_O + r_{O_2} V - N_{O_2} \quad \text{(for oxygen } O_2\text{)}$$

Figure 11, shown previously, illustrates the material balance equations presented above and provides a comparison with the Hwang (1980) model. Note that the substrate material balance given above does not consider substrate lost to wasted sludge.

Mass Transfer--

Freeman also employs Thibodeaux's aerated surface impoundment model for predicting the air stripping losses based on mass transfer at the air-water interface. Like Hwang, Freeman isolates zones for convective and turbulent mixing and applies appropriate mass transfer expressions for each. The final form of Freeman's mass transfer expression describing the stripping of a substrate X_a from an AS reactor is shown below:

$$N_a = \left[\frac{N \pi D^2}{4} K_a^{\ T} (X_a) + \left(A_s - \frac{N D^2}{4}\right) K_a^c X_a\right] MW_a$$

Freeman used similar analogies to predict the rate of oxygen transfer into the AS basin as:

$$N_{O_2} = \left[\frac{N \pi D^2}{4} K_b^{\ T} \left(X_{O_2}^* - X_{O_2}\right) + \left(A_s - \frac{N\pi D^2}{4}\right) K_b^c \left(X_{O_2}^* - X_{O_2}\right)\right] MW_{O_2}$$

Note that in Freeman's formula the turbulent area is given as $\pi D^2/4$ where D is the diameter of the region of effect for a given surface aerator. Estimates on regions of turbulence for various sized surface aerators were presented earlier in Section 4. Essentially, all aspects of the mass transfer expression given above are identical to that in the Hwang ASSA model.

Biokinetics--

To represent the biological oxidation process, Freeman selected a model developed by Gerber et al. (1976) as shown below:

$$B + A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} BA$$

$$BA + O_2 \underset{k_4}{\overset{k_3}{\rightleftharpoons}} BAO_2$$

$$BAO_2 \xrightarrow{k_5} B + P$$

where:

B = micro-organisms;

A = substrate;

O_2 = dissolved oxygen;

P = products.

Assuming that the last step is rate determining, and the basin is completely mixed, Freeman predicts the rate of oxygen uptake as:

$$r_{O_2} = \frac{k_5\, B_o\, C_o\, O_o}{\frac{k_5}{k_1} O_o + K_{O_2} K_S + C_o O_o + K_{O_2} C_o}$$

where:

$K_{O_2} = (k_4 + k_5)/k_3$

$K_S = k_2/k_1$.

In relating the oxidation of compound A to oxygen uptake and biomass growth, Freeman writes the following:

$$t\, O_2 + s\, A \rightarrow B + H_2O + CO_2 + \text{products}$$

where:

t and s are stoichiometric constants based on assumptions made about the molecular structure of the biomass in the above equation.

Based on the above equation, the rate of biomass growth (r_B) and the rate of substrate (compound A) removal (r_A) can be shown as follows:

$$r_B = t \quad r_{O_2}\left(\frac{MW_B}{MW_{O_2}}\right)$$

$$r_A = \frac{t}{s} \quad r_{O_2}\left(\frac{MW_A}{MW_{O_2}}\right) .$$

Thus, the final expression for the rate of substrate utilization would be:

$$r_A = \frac{t \; k_5 \; B_o \; C_o \; O_o}{\left(s \;\; \frac{k_5}{k_1} \; O_o + K_{O_2} \; K_S + C_o \; O_o + K_{O_2} \; C_o\right)}\left(\frac{MW_A}{MW_{O_2}}\right).$$

Similarly, Freeman's expression for the value of biomass growth would be:

$$r_B = \frac{t \; k_5 \; B_o \; C_o \; O_o}{\left(\frac{k_5}{k_1} \; O_o + K_{O_2} \; K_S + C_o \; O_o + K_{O_2} \; C_o\right)}\left(\frac{MW_B}{MW_{O_2}}\right).$$

Model Solution

Solution of the above system of equations requires the following data:

- process flow rates (feed, recycle, effluent) and basin dimensions;
- physical data and energy input data for calculating mass transfer coefficients;
- biokinetic rate constants for the compound being considered (which can be obtained by methods discussed later).

One key difference between the solution method for Freeman's ASSA model and the Hwang ASSA model presented earlier is the extent of data assumed to be known at the start of the problem. The Hwang model works with a known biomass concentration and assumes that sufficient oxygen is maintained in the aeration basin to support biological growth. On the other hand, Freeman's model considers the interaction of the substrate (the compound being removed), biomass, and oxygen material balances, thus Freeman's model can be used to predict emissions when less information is known. However, the solution procedure for Freeman's model is inherently more difficult, as it requires the solution of three simultaneous nonlinear equations to determine three unknowns (B_o, C_o, and O_o) by iterative method. The solution method is briefly outlined in Table 37. Freeman recommends that the solution be conducted by application of a small personal computer. Computerized solution will tend to save time and calculational errors will be avoided.

TABLE 37. SOLUTION METHOD FOR FREEMAN's ACTIVATED SLUDGE SURFACE AERATION AERR MODEL

1. Determine mass transfer coefficients and effective areas of turbulence and convection. (Discussed in detail in Section 4, Surface Impoundments).
2. Estimate Stoichiometry of Biological Decomposition of Compound A to products to determine values of stoichometric constants t and s in the following equation:

   $t\ O_2 + s\ A \rightarrow B + H_2O + CO_2 + \text{Products}$

3. Obtain biokinetic rate constants through laboratory tests (see text).
4. Write Material Balance Equation for substrate, micro-organisms, and oxygen as below:

For substrate balance

$$C_I F_I + F_r C_r = C_0 F_0 + \overbrace{\left[N\ \frac{\pi D^2}{4}\ K_a^T\ (X_a) + \left(A_S - \frac{N\pi D^2}{4}\right) K_a^c\ X_a\right]}^{N_a} MW_a + \overbrace{\left[\frac{t}{s}\ \frac{K_5\ B_0\ C_0\ O_0}{\left(\frac{k_5}{k_1}\ O_0 + K_{O_2}\ K_S + C_0\ O_0 + K_{O_2}\ C_0\right)}\ \frac{MW_a}{MW_{O_2}}\right]}^{r_a} V$$

where $X_a = C_0 \left(\frac{MW_{H_2O}}{MW_a}\right) \frac{1}{\rho_{H_2O}}$

For micro-organism balance

$$B_I F_I + F_r B_r = B_0 F_0 - \overbrace{\left[t\ \frac{k_5\ B_0\ C_0\ O_0}{\left(\frac{k_5}{k_1}\ O_0 + K_{O_2}\ K_S + C_0\ O_0 + K_{O_2}\ C_0\right)}\ \frac{MW_B}{MW_{O_2}}\right]}^{r_b} V$$

For oxygen balance

$$O_I F_I + F_r O_r = O_0\ F_0 + \overbrace{\left[\frac{k_5\ B_0\ C_0\ O_0}{\frac{k_5}{k_1}\ O_0 + K_{O_2}\ K_S + C_0\ O_0 + K_{O_2}\ C_0}\right]}^{r_{O_2}} V - \overbrace{\left[N\ \frac{\pi D^2}{4}\ K_b{}^T\left(X_{O_2}^* - X_{O_2}\right) + \left(A_s - \frac{N\pi D^2}{4}\right) K_b{}^c \left(X_{O_2}^* - X_{O_2}\right)\right]}^{N_{O_2}} MW_{O_2}$$

where $X_{O_2} = O_0 \left(\frac{MW_{H_2O}}{MW_{O_2}}\right) \frac{1}{\rho_{H_2O}}$

5. Select valves for B_0, C_0, and O_0 and solve the material balance equations. Repeat as necessary until the solution converges.

Biokinetic Rate Constant Determination--

According to Freeman, determination of biokinetic rate constants to fit the Gerber kinetics model can be conducted in one of two ways. By following the work of Gerber, laboratory experiments can be conducted at considerable cost and the data may be plotted to directly determine Gerber's rate constants. Freeman estimates that this method could cost in the range of $50,000 to $100,000 per compound to develop the appropriate kinetics data. The cost would tend to be dependent on the compounds characteristics (biodegradability, volatility, etc.).

Another method used by Freeman in experiments with acrylonitrile (AN) involved calibration of the entire model based on laboratory experiments measuring feed AN and AN emissions. In order to apply this calibration method Freeman measured or calculated all variables in the equations shown in Table 37 except the biokinetic rate constants. The rate constants were then determined by "fitting" the model predictions to the measured results under varying conditions. One drawback to this method was that Freeman apparently assumed Gerber's values for k_{O_2} and k_B were applicable to AN biokinetics. While Freeman's assumption may or may not be correct, the model should be accurate at least within the range of testing done by Freeman.

Freeman (1980) Diffused Air (Subsurface) Activated Sludge Model

In later work Freeman (1980) developed a significant modification to the initial AS model to more adequately describe the mass transfer phenomena taking place in diffused air AS systems. Diffused air systems are commonly employed in laboratory bench testing and occasionally used in actual field applications. Freeman's Diffused Air Activated Sludge (DAAS) model, also called the subsurface aeration model, focuses on the mass transfer of the compound into the air bubbles released by the spargers as the bubbles rise to the surface. This is quite different from the models discussed earlier, since the area across which mass transfer takes place is the surface area of the bubbles, not the basin surface area. Note that this model is better suited to the activated sludge diffused air application than other models discussed. Aside from the variation in mass transfer expressions the DAAS model should be considered identical to Freeman's earlier AS model, thus only mass transfer aspects of the model will be discussed.

Mass Transfer--

If it is assumed that the concentration of compound i in the air diffuser source is negligible, than Freeman's expression for the concentration of compound i in an air bubble as it reaches the surface is:

$$y_2 = m X_i \left[1 - \exp\left(\frac{-6 k_x \theta MW_{air}}{D_B \rho_g m} \right) \right]$$

where:

m = distribution coefficient;

X_i = mole fraction of compound i in liquid (ppm);

k_x = overall mass transfer coefficient to the bubble from the liquid (g-mole/hr-cm^2);

θ = rise time of bubbles (hours);

MW_{air} = molecular weight of air (28.8 g/g-mol);

D_B = mean bubble diameter (cm);

ρ_g = density of air (g/cm^3);

y_2 = mole fraction of compound i in the gas bubble as it breaks the surface.

The mean bubble diameter required above may be estimated according to the following equation by Calderbank (1967):

$$D_B = 4.15 \left[\frac{\sigma^{0.6}}{(P/V)^{0.4} \; \rho_1^{0.2}} \right] \Psi^{1/2} + 0.09 \text{ cm}$$

where:

σ = liquid surface tension (g/s^2);

ρ_1 = liquid density (g/cm^3);

P/V = power input to liquid per unit volume of basin (g-cm^2/s^3-cm^3);

Ψ = gas holdup fraction in basin.

The power input per unit volume (P/V) to the basin could be estimated from diffuser system power use or from the superficial gas velocity as follows:

$$P/V = V_G \, \rho_1 \, g$$

where:

V_G = superficial gas velocity (cm/s);

g = acceleration due to gravity (980.6 cm/s^2).

The gas holdup fraction is estimated by Towell (1965) as:

$$\Psi = \frac{V_G}{0.9 + 2 \, V_G}$$

Note that V_G is simply the gas volumetric flow rate divided by the surface area of the tank and 0.9 is an approximation of the terminal gas velocity (V_t) in feet per second.

In the application of the above described diffusional air mass transfer model, Freeman assumes the overall transfer is controlled by the liquid film. Thus:

$$\frac{1}{K_x} = \frac{1}{mk_g} + \frac{1}{k_l} = \frac{1}{k_l} \text{ for large value of } k_g .$$

Freeman uses Calderbank's (1967) relationship for the liquid film mass transfer coefficient in the following form:

$$k_l \, (Sc)^{1/2} = 0.42 \left[\frac{(\rho_l - \rho_g) \, \mu_l g}{\rho_l^{\,2}} \right]^{1/3} (3600) \frac{\rho_l}{MW_{H_2O}} .$$

Other Activated Sludge Models

Among the numerous other efforts in modeling air emissions from the AS process, the work of Wukash et al. (1981), and Brown and Weintraub (1982) should be referenced for completeness.

Publicly Owned Treatment Works (POTWs)--

Work conducted by Wukash et al. (1981), describing the fate of organic compounds in POTWs, presents a systematic approach towards model development. This study found, as did Hwang, that air stripping, biodegradation and adsorption to biomass were mechanisms associated with pentachlorophenol (PCP) removal in the AS process. Air stripping was found to be responsible for removal of less than 0.04 percent of the PCP applied, while adsorption onto biomass accounted for less than 0.3 percent of the PCP. Important conclusions of this study are summarized below:

- At substrate concentrations below the inhibitory threshold, the equilibrium concentration of a growth limiting substrate can be described by Monod kinetics as follows:

$$\mu = \frac{\mu_m S}{K_s + S}$$

where:

μ = specific cell growth rate (day $^{-1}$);

μ_m = maximum growth rate achievable;

K_s = saturation constant (mg/l);

S = substrate concentration (mg/l) also [S_e (Hwang)] or [C_o (Freeman)].

- At much lower substrate concentrations ($S < < K_s$), as is the case for most POTWs, the Monod equation reduces to simple first order kinetics:

$$\mu \cong \frac{\mu_m S}{K_s}$$

Under steady state conditions μ is equal to the reciprocal of the sludge retention time (1/SRT) plus decay (d) thus:

$$\mu = 1/SRT + d = \frac{\mu_m S}{K_s}$$

rearranging:

$$S \cong \frac{K_s}{\mu_m} (1/SRT) + \frac{K_s d}{\mu_m}$$

Wukash et al., found very good correlation with first order kinetics shown above for PCP concentrations below inhibitory levels (< 350 µg/l).

Point Process Wastewater Treatment--

A study done by Brown and Weintraub (1982) indicated that the rate of substrate removal could be predicted by pseudo first order kinetics of the following form:

$$\text{removal rate} = \frac{S_o - S_e}{X_v\ t} = k\ S_e$$

where:

S_o = influent COD concentration;

S_e = effluent COD concentration;

X_v = mixed liquor volatile suspended solids (MLVSS);

Q = flow rate;

V = reactor volume;

t = residence time = V/Q;

k = coefficient of substrate removal.

The laboratory results from testing several paint process water constituents apparently fit the model shown above extremely well. Substrate concentrations ranged up to 600 ppm in some tests.

The results of the above investigations were included to illustrate the point that one single biokinetic model may not be the only model capable of fitting biodegradation rate data. Furthermore, the number of biokinetic rate expressions is almost as vast as the number of investigators conducting research. No single biokinetic model is currently viewed as the best model, although the Monod model and first order models have been in general use for some time.

As noted earlier, Hwang investigated four biokinetic models before selecting Grau kinetics for use in his model. He expressed concern (Hwang 1982) that a model for complete mix systems would be based on the influent concentration. While this is contrary to basic assumptions for complete mixed reactors [Rx is usually $f(S_e)$], Hwang notes that it apparently works better than other commonly accepted models.

Similarly, Freeman (1982) noted that in his modeling work various biokinetic rate expressions are commonly employed to determine "best fit" to the data. Freeman indicates that any reasonable biokinetic model could be employed using his modeling approach. Freeman selected the Gerber model for its ability to consider the interaction of the substrate balance, the biomass growth balance, and the oxygen balance. However, Freeman also notes that Gerber's (1976) model can reduce to Monod kinetics by assuming constant biomass concentration and sufficient oxygen.

Selection of Biological AERR Model

The selection of an appropriate AS model or models for predicting emissions of organic compounds should be based upon the following criteria:

- model flexibility;
- simplicity;
- model accuracy;
- underlying assumptions.

The following discussion will focus on the above issues, briefly presenting the relative merits of the models presented earlier.

Model Flexibility--

In order to assess the extent to which models are adequately flexible, it is necessary to understand the circumstances for which they were intended and those for which we wish to apply them. Consider the application of; (1) the Thibodeaux aerated surface impoundment (ASI) model; (2) the Hwang activated sludge surface aeration (ASSA) model; (3) the Freeman ASSA model; and (4) the Freeman diffused air activated sludge (DAAS) model. These models run the gambit from the simple ASI model which requires a known concentration of compound i in the aeration basin, to the Freeman DAAS model which can relate emissions to a wide range of plant design and operating parameters.

Engineers working for regulatory agencies or consultants may desire to assess emissions from planned and existing facilities. Conventional surface aerator design lagoons will be prevalent, however, energy efficient DAAS systems may also be encountered. The ability of each of the four models to predict emissions under varying circumstances is shown in Table 38. As shown in Table 38, the Hwang ASSA Model tends to be very flexible except in predicting emissions from oxygen limited systems, or systems operating under unconventional circumstances. Of course, only the Freeman DAAS model adequately handles circumstances involving diffused air systems. Note that where sludge adsorption is determined to be substantial only the Hwang ASSA model is adequate. In addition, the Hwang model also finds greater immediate application to many organic compounds because adequate biokinetics rate data have been developed for the Hwang (Hwang 1980) model as compared to the Freeman ASSA Model.

Model Simplicity--

One underlying problem in predicting AERR from the AS process is the complex nature of the solution method required. In comparison to other AERR models, the AS models are among the most complex to solve. The Thibodeaux ASI model is, of course, relatively simple, whereas the Freeman ASSA and DAAS models requires the assistance of a small computer for practical purposes. A somewhat subjective ranking of the complexity of the models on a scale of 1 to 10 (10 being the most complex solution) is given below:

Model	Complexity rating
Thibodeaux ASI	1
Hwang ASSA (without sludge adsorption)	2
Hwang ASSA (with sludge adsorption)	4
Freeman ASSA	8
Freeman DAAS	10

Realizing that most of the AS models presented require time consuming solution techniques, the Hwang ASSA model with sludge adsorption is probably the most complex model an evaluator could be expected to employ without the aid of a small computer.

The issue of model simplicity must be viewed with regard to problem application. For example, given the concentration of compound i (S_e) in the aeration basin, the ASI model is the logical, simple choice. Use of other models under these circumstances would be poor judgement and likely lead to conflicting information. Similarly, application of the Freeman ASSA model for a compound for which no biodegradation kinetics data have been generated would be difficult. However, use of any ASSA model to predict diffused aerator emissions would be in error. Thus, in this case, the additional complexity of Freeman's subsurface diffused air mass transfer expression is justifiable. Also, the increased complexity of Freeman's ASSA model is justifiable for very high substrate loading conditions, or for modeling an oxygen starved reactor.

TABLE 38. APPLICATION OF VARIOUS ACTIVATED SLUDGE AERR MODELS

	Applications					
	Surface aeration					Diffused aeration
Model	Given: S_e only	Given: S_o conventional system	Given: S_0 Oxygen limited	Given: S_0 Process upset	Given: S_o substrate adsorbtion	All conditions
Thibodeaux ASI	X					
Hwang ASSA	X	X			X	
Freeman ASSA	X	X	X			
Freeman DAAS	X					X

It is doubtful that such model flexibility will be required for modeling air emissions from planned facilities on a regular basis. While Freeman's models do have valuable use under certain circumstances, it is clear that they were developed for research and design purposes rather than fulfilling analytical needs.

Model Accuracy--

The Thibodeaux ASI model was tested by Cox, et al. (1982) and shown to underpredict benzene emissions as indicated in Section 3. However, it was noted by Hwang* that calculational errors were made in assuming application of Raoult's Law. When applying Henry's Law, the corrected model predictions were found to be within a factor of 2 to 3 to the measured results. Additional model verification was also conducted by Thibodeaux (1981) for methanol. These measured results showed reasonable agreement with predicted emissions.

Tests conducted for the Thibodeaux ASI model are largely applicable to the mass transfer portion of the Hwang ASSA models since they are identical in this respect. Freeman's ASSA model also employs the same mass transfer terms and would be similar in accuracy. Biokinetic rate data and sludge adsorption data were collected for input to the Hwang model. No complete testing of the fully assembled model has been conducted to date. However, if the individual elements are based on test data it can be rationalized that the total model should be reliable.

Freeman (1980, 1982) also conducted laboratory experiments to verify the mass transfer portions of his DAAS model separate from the biokinetics model. Using air stripping experiments with sterile reactors, Freeman (1980) found that the subsurface diffused air model predicted the material balance for acrylonitrile to within 3.2 percent. Freeman (1982) also calibrated the Gerber biokinetics model, using the DAAS mass transfer model, for acrylonitrile and for other organic compounds.

Model Assumptions--

Complete Mix Reactor--One basic underlying assumption of all the models investigated is the complete mix reactor assumption. This assumption is basic to most conventional AS process modeling and will not be disputed. However, GCA notes that there may exist some contradiction between the complete mix modeling assumption and the turbulent/convective zone mass transfer concept used in the ASI and ASSA models. In reviewing these models, GCA questioned the necessity of considering the convective zone mass transfer since the transfer from the turbulent zone should be substantially greater. However, Hwang* pointed out that for large area lagoons the area of convective mass transfer could be very large (inferring low mixing might result). Thus, in this application the complete mix assumption may not be completely accurate.

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*Telecon with Tom Nunno of GCA, 15 September 1982.

Mass Transfer--Assumptions regarding the governing mechanisms of mass transfer are summarized as follows:

- ASI and ASSA models reviewed assume that mass transfer takes place at the surface according to the two-film resistance theory. In addition, these models generally assume that the concentration of compound i (X_i) in the air is neglibible to that in the liquid.
- Freemans DAAS model assumes that mass transfer takes place at the diffused air bubble interface and that, again, the initial concentration (X_i) is zero and increases until equilibrium is reached. The Freeman DAAS model also assumes that the overall mass transfer rate (K_L) is equal to the liquid phase mass transfer coefficient (k_l) because the gas phase mass transfer coefficient is assumed to be very large. In addition, the DAAS model assumes that mass transfer which takes place at the surface is small compared to subsurface mass transfer and, thus, is negligible.

Biokinetics Model--The biokinetic rate expressions employed in the Hwang and Freeman models are quite different in structure, complexity, and underlying assumptions. The Hwang model relies on Grau kinetics which assumes adequate oxygen in the basin. The Freeman model uses Gerber kinetics which considers oxygen requirements in the biokinetic expression. As mentioned earlier, it is difficult to judge the relative merits of biokinetic models. However, it is likely that the Gerber model would be valid under a greater range of conditions than the Grau model.

Sludge Adsorption--Only the Hwang ASSA Model considers adsorption of substrate to the sludge competing with other substrate removal mechanisms. Freeman's ASSA and DAAS models both assume that adsorption of substrate is negligible. While this assumption may be valid for many organic compounds based on the work of Kincannon, adsorption has been shown to be significant in several instances (Hwang 1981, Patterson 1981).

Model Selection

The Hwang ASSA model is preferred to Freeman's model because the Hwang model is most easily applied, employs simpler bioxidation kinetics for which rate constant data is available, and is capable of modeling adsorption of substrate to the biomass. Freeman's DAAS mass transfer equations are recommended for modeling diffused air systems because they are currently the only reasonable choice. The DAAS mass transfer equations could be integrated into Hwang's ASSA model for predicting DAAS air emission release rates where the effluent concentration is unknown. This is recommended to simplify the problem solution and to avoid costly data collection required to use Freeman's biokinetic model.

Based on the factors discussed above GCA recommends that EPA select the following models for the applications listed below:

Application	Selected model
Surface aeration--effluent or aeration basin concentration (S_e) known	Thibodeaux ASI model
Surface aeration--influent concentration (S_o) known	Hwang ASSA model
Diffused aeration--S_e known	Freeman DAAS model
Diffused aeration--S_o known	Hwang (modified after Freeman)

The basis for selecting the Thibodeaux ASI and Hwang ASSA models for applications to surface aerated treatment systems includes considerations of simplicity, accuracy and ease of application. It is believed that these models will adequately predict emissions from the majority of most AS treatment systems and are acceptable for use by most permitting engineers. In addition, the availability of biokinetic rate data for Grau kinetics makes the Hwang ASSA model particularly attractive for general use. Because the Hwang ASSA model does not apply well to subsurface diffused air systems, it is recommended that for modeling diffused air systems the Hwang model be modified to incorporate diffused air mass transfer mechanisms similar to that described by Freeman (1980). Freeman's diffused air mass transfer model could be incorporated into the Hwang model without substantial effort. This modification would permit the application of Freeman's mass transfer expression integrated with the Grau kinetics and sludge adsorption considerations of Hwang's model.

SECTION 9

AIR EMISSIONS FROM DRUM STORAGE AND HANDLING FACILITIES

INTRODUCTION

Drum storage and handling facilities encompass diverse operations and sources of air emissions. Sources of routine air emissions include the storage of volatiles in lagoons or storage tanks. Air emission release rate estimation techniques for these activities are described in other sections of this report. The other important air emissions category is thought to be accidental spills.

The purpose of this section is to identify data necessary for estimating air emissions attributed to accidental spills at drum storage and handling facilities. This section provides a general description of a drum storage and handling facility and also some spill rate data for hazardous waste treatment facilities and petroleum handling facilities. At present, no data specific to air emissions from drum handling and storage facilities have been found.

DESCRIPTION OF DRUM STORAGE AND HANDLING FACILITIES

At drum storage and handling facilities, waste material, most commonly solvents, may arrive by tank car or tank truck, as well as in drums. Material may then be pumped to storage tanks, lagoons, or other drums for storage. Materials are segregated by type until enough are collected for reprocessing or disposal either onsite or offsite with removal again either by tank car, or tank truck, and less commonly, in drums.

Drums are removed from a tractor trailer on arrival with a fork lift and are conveyed to and from the drum storage building, ideally a locked metal building with louvered gables where storage occurs on concrete pads. Drums which are stored directly on the ground may freeze to the surface, thus, are subject to rupture during removal.

A number of other operations may also occur. Damaged drums will usually be replaced either upon arrival or upon later inspection. Material may have to be resampled to check compatibility parameters such as flash point, acidity or chloride content. Drums may be intentionally burst if this is the most effective way of removing contents of damaged barrels.

SOURCE OF VOLATILE AIR EMISSIONS

It is useful to classify emissions as routine or accidental, and to further classify routine emissions as either continuous or intermittent. Examples of each category are shown in Table 39. Note that routine continuous air emissions are from sources (lagoons and storage tanks) for which air emission release rate models have been previously discussed. It also appears that intermittent routine emissions cannot be very significant since they involve only one drum at a time over limited time periods.

To describe total facility emissions there are two approaches depending on available data:

- Total facility emissions, in barrels* lost per barrel handled;
- With an accurate description of onsite lagoons and storage tanks, air emissions from these sources can be calculated directly and then supplemented by the accidental spill rate, again parameterized by barrels lost per barrel handled.

The remainder of this discussion assumes the second course.

LITERATURE SURVEY

No examples have been found in the literature corresponding directly to spill rate data at drum storage and handling facilities. Nevertheless, we mention some recent work which is relevant.

Hillenbrand, et al. (1982) have surveyed Pollution Incident Reporting System (PIRS) and Spill Prevention, Control, and Countermeasures (SPCC) data for EPA. The study is restricted to tank farms and chemical plant tanks greater than 100,000 gallons. Data consists mainly of gasoline and fuel oil, but also includes spill reports on non-fuel products, organic and inorganic materials. The report categorized over 3,000 spills by cause (pipe rupture, pipe malfunction, etc.) and quantity. Unfortunately, they have not been able to give a spill rate based on the total amount of material handled (i.e., "exposure variable").

Also under EPA contract, ICF, SCS and Clement Associates (1982) have surveyed release rates and costs for waste treatment technologies. As part of this work, estimates were made of routine and accidental spillage based apparently on "best judgment." Some loss fraction estimates for accident spills for various treatment processes are shown in Table 40.

This report also notes that a December 1980 study by F. G. Bercha and Associates estimated a spill loss fraction of 2.45×10^{-4} for hazardous waste loading and unloading operations.

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*The term barrels is used in this section as a unit of volume whether or not material is in drums, tanks, etc.

TABLE 39. EXAMPLES OF ROUTINE AND ACCIDENTAL SPILL SITUATIONS AT A DRUM STORAGE AND HANDLING FACILITY

Routine	Accidental
Continuous	
• Lagoon emissions	• Drum rupture by transfer operations
	• Dropped drum
• Storage tank breathing and working losses	• Tank or drum overflow
	• "Spontaneous" drum failure
Intermittent	• Pipe rupture or pump malfunction
• Open pouring	
• Sampling open drums	• Faulty hose coupling
• Intentional drum bursting	

TABLE 40. ACCIDENTAL SPILL FRACTIONS FOR VARIOUS TREATMENT TECHNOLOGIES[a]

Technology	Accidental spill fraction (amount spilled/ amount handled)
Chemical stabilization	1.5×10^{-3}
Chemical precipitation	2.6×10^{-4}
Chemical destruction	1.1×10^{-5}
Chemical coagulation	2.6×10^{-4}
Filter press	1.1×10^{-4}
Centrifuge	2.2×10^{-4}
Vacuum filter	1.1×10^{-4}
Evaporation	7.7×10^{-4}
Air stripping	1.3×10^{-4}
Steam stripping	2.1×10^{-4}
Solvent extraction	1.6×10^{-4}
Leaching	3.0×10^{-4}
Distillation	2.1×10^{-4}
Electrolytic decomposition	2.2×10^{-4}
Reverse osmosis	1.9×10^{-4}
Carbon adsorption, PAC	4.3×10^{-4}
Ion exchange	4.3×10^{-9}
Average	3.0×10^{-4}

[a] From "RCRA Risk/Cost Policy Model Project;" ICF, Inc., SCS Engineers, Inc., and Clements Associates, Inc., 1982.

Murphy, et al. (1981) presented data for oil spills occurring at the Milford Haven Terminal over an 18-year period. The loss fraction attributable to terminal operations (faulty hose couplings, pumps, valves, etc.) are 4×10^{-5}.

Until we have the pertinent data in hand we cannot confirm that any of the figures above are relevant to drum handling and storage facilities. Yet these figures do represent what is considered acceptable in operations with a number of similar steps. Our best estimate, therefore, is that the spill rate at drum handling and storage facilities is between 1 and 100 barrels per 100,000 barrels handled.

OTHER CONSIDERATIONS

The amount spilled is not the same as the amount of volatile released to the atmosphere. Absorbent material will be added, at least to significant spills, when spills are discovered during inspection. Spills on a concrete surface, as opposed to ground, will be more amenable to cleanup. Since individual spills occur randomly, spills that are not noticed at the time of the occurrence will tend to grow in number linearly with time in the interval between inspecton periods.

Many handling operations occur in outdoor areas. The rate at which material volatilizes before it can be cleaned up will then depend on temperature and wind conditions. Similarly, for indoor spills, volatilization rates will depend primarily on temperature and ventilation conditions. Finally, human factors such as management attitudes and worker training and indoctrination must be important in determining the accidental spill rate.

SECTION 10

PARTICULATE EMISSIONS ESTIMATION TECHNIQUES FOR WASTE PILES

INTRODUCTION

Particulate air emissions from waste piles occur at several points in the storage cycle:

- transfer of material to and from the pile;
- wind erosion;
- maintenance and traffic activities on the pile.

Particulate emissions from waste piles are influenced by the following factors:

- moisture content;
- rainfall;
- duration of storage;
- compaction of pile;
- amount and size of aggregate fines.

A method of estimating particulate emissions from waste piles is available in EPA publication AP-42. Cuscino, et al. (1981) presents emission factor equations empirically developed by Midwest Research Institute (MRI). Both methods describe emissions of particles smaller than 30 μm in diameter based on a particle density of 2.5 g/cm^3.

AP-42 EMISSION FACTOR EQUATION FOR STORAGE PILES

The quantity of suspended particulate emissions from waste piles may be estimated by the following equation:

$$E = \frac{0.33}{\left(\frac{PE}{100}\right)^2}$$

where: E = emission rate, pounds per ton of material placed in storage;

PE = Thornwaite's precipitation - evaporation index from Figure 12.

This equation only considers geographic variations in precipitation/evaporation. Emission factor equations developed by MRI based on test data allow for variances in facility operations.

MRI EMISSION FACTOR EQUATIONS FOR STORAGE PILES

The emission factor equations empirically developed by MRI for uncontrolled storage piles are shown in Table 41. These equations were developed from limited testing of storage piles at iron and steel facilities (i.e. coal, iron pellets, coke, slag, etc.). However, the use of these predictive equations may provide for greater accuracy than the single value emission factor equation (from AP-42). Input parameters for the MRI equations account for source variability.

The diversity of materials handled and differences in handling operations suggest that additional source testing may increase the precision of the predictive equations. The estimation accuracy for the storage pile maintenance and storage pile wind erosion equations are unknown due to limited test data.

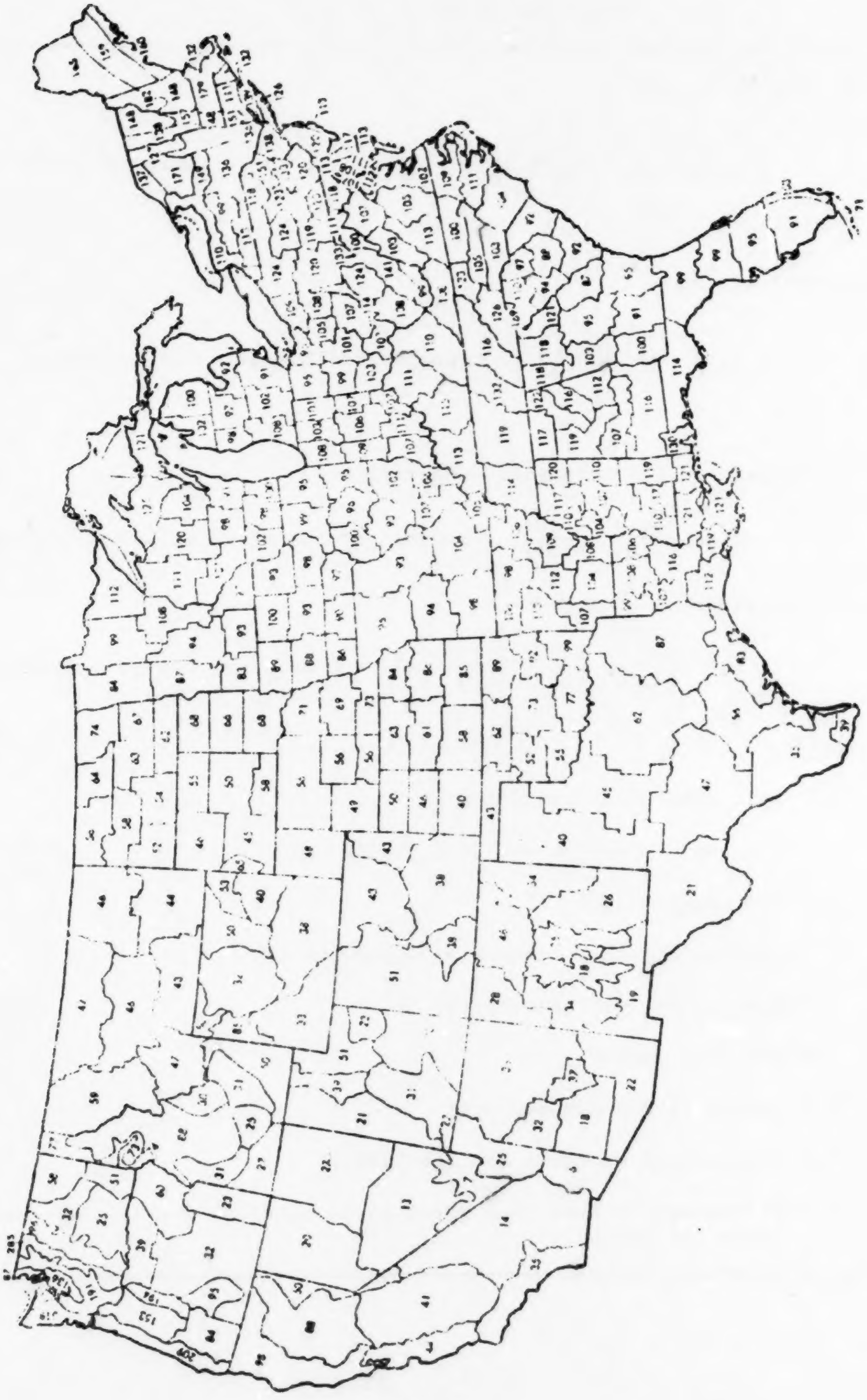

Figure 12. Map of Thornthwaite's Precipitation-Evaporation Index values for state climatic divisions. (From AP-42).

TABLE 41. STORAGE PILE PARTICULATE EMISSION FACTOR EQUATIONS DEVELOPED BY MRI

Batch load-in or load-out:

$$0.0018 \frac{\left(\frac{s}{5}\right)\left(\frac{u}{5}\right)\left(\frac{h}{5}\right)}{\left(\frac{M}{2}\right)^{2}\left(\frac{Y}{6}\right)^{0.33}} = \text{pounds per ton of material transfered}$$

Continuous load-in:

$$0.0018 \frac{\left(\frac{s}{5}\right)\left(\frac{u}{5}\right)\left(\frac{h}{10}\right)}{\left(\frac{M}{2}\right)^{2}} = \text{pounds per ton of material loaded}$$

Active storage pile maintenance and traffic:

$$0.10K \left(\frac{s}{1.5}\right)\left(\frac{d}{235}\right) = \text{pounds per ton of material put through storage}$$

Active storage pile wind erosion:

$$0.05 \left(\frac{s}{1.5}\right)\left(\frac{d}{235}\right)\left(\frac{f}{15}\right)\left(\frac{D}{90}\right) = \text{pounds per ton of material put through storage}$$

Parameters

s = silt content of aggregate (%)

u = mean wind speed at 4m above ground (mph)

h = drop height (ft)

M = unbound moisture content of aggregate (%)

Y = dumping device capacity (cu. yd.)

K = activity factor

d = number of dry day per year

D = duration of material storage (days)

f = percentage of time wind speed exceeds 12 mph measured at one foot above the ground.

APPENDIX A

REFERENCES

American Petroleum Institute, Evaporation Loss Committee. Evaporation Loss from External Floating Roof Tanks. Bull. 2517 (revised), Washington, DC, February 1980.

American Petroleum Institute, Evaporation Loss Committee. Evaporation Loss from Fixed Roof Tanks. Bull. 2518, Washington, DC, June 1962.

American Petroleum Institute, Evaporation Loss Committee. Evaporation Loss from Internal Floating Roof Tanks. Bull. 2519 (revised), Washington, DD, June 1983.

Ames, et al. Suggested Control Measure to Reduce Organic Compound Emissions Associated with Volatile Organic Waste Disposal. Air Resources Board, State of California, Industrial Strategy Development Branch. August 20, 1982.

Arnold, J. H., Unsteady-State Vaporization and Absorption. Transaction of American Institute of Chemical Engineers 40, 361-379. 1944.

Ball, B. C., W. Harris and J. R. Burford. A Laboratory Method to Measure Gas Diffusion and Flow in Soil and Other Porous Materials. Journal of Soil Science, 32. 1981.

Brown, J.A. and M. Weintraub. Bioxidation of Paint Process Wastewater. Journal WPCF, Vol. 54, No. 7, pp. 1127-1130, July 1982.

Calderbank, P. H. "Mass Transfer," Chapter 6 of Mixing, edited by V. W. Uhl and J. B. Gray, Academic Press, New York, 1967.

Chicago Bridge and Iron Company, Plainfield, IL. Hydrocarbon Emission Loss Measurements on a 20 foot Diameter Pilot Test Tank with an Ultraflote and a CBI Weathermaster Internal Floating Roof. R-0113/R-0191, June 1978.

Cohen, Yoram, William Cocchio and Donald Mackay. Laboratory Study of Liquid Phase Controlled Volatilization Rates in Presence of Wind Waves. Environmental Science and Technology, Vol. 12, No. 5. May 1978.

Conway, Richard A. (ed), Environmental Risk Analysis for Chemicals. Van Nostrand Reinhold Company, New York, 1982.

Compilation of Air Pollutant Emission Factors (AP-42), U.S. Environmental Protection Agency. Research Triangle Park, N.C. April 1981.

Cox, Robert D., Jana L. Steinmetz and David L. Lewis. Evaluation of VOC Emissions from Wastewater Systems (Secondary Emissions), Draft Report. Radian Corporation. July 1982.

Currie, J. A. Gaseous diffusion in porous media. Part 2 - Dry Granular Materials. British Journal of Applied Physics, Vol. 11. August 1960.

Currie, J. A. Gaseous diffusion in porous media. Part 3 - Wet Granular Materials. British Journal of Applied Physics, Vol. 12. June 1961.

Cuscino, Thomas A. Jr., Chatten Cowherd, Jr., and Russel Bonn. Fugitive Emission Control of Open Dust Sources. Proceedings: Symposium on Iron and Steel Pollution Abatement Technology for 1980. EPA-600/9-81-071. March 1981.

Danielson, John A. Air Pollution Engineering Manual, AP-40. U.S. Environmental Protection Agency, Research Triangle Park, NC, May 1973.

Dilling, Wendell L., Nancy B. Tefertiller, and George J. Kallos. Evaporation Rates and Reactivities of Methylene Chloride, Chloroform, 1,1,1-Trichloroethane, Trichloroethylene, Tetrachloroethylene, and other Chlorinated Compounds in Dilute Aqueous Solutions. Environmental Science and Technology, Vol. 9, No. 9. September 1975.

Dilling, Wendell L. Interphase Transfer Processes II. Evaporation Rates of Chloro Methanes, Ethanes, Ethylenes, Propanes, and Propylenes from Dilute Aqueous Solutions. Comparisons with Theoretical Predictions. Environmental Science and Technology, Vol. 11, No. 4. April 1977.

Ehlers, Wilfried, J. Letey, W. F. Spencer and W. J. Farmer. Lindane Diffusion in Soils: I. Theoretical Consideration and Mechanism of Movement, Soil Science Society American Proceedings, 33. 1969.

Erikson, D.G. Organic Chemical Manufacturing, Volume 3: Storage, Fugitive and Secondary Sources. EPA-450/3-80-025. Research Triangle Park, NC, December 1980.

Farmer, Walter J., M. S. Yang and J. Letey. Land Disposal of Hazardous Wastes: Controlling Vapor Movement in Soils. Fourth Annual Research Symposium. EPA-600/9-78-016. August 1978.

Farmer, Walter J., Ming-Shyong Yang, and John Letey. Land Disposal of Hexachlorobenzene Wastes: Controlling Vapor Movement in Soils. EPA-600/2-80-119. August 1980.

Freeman, R. A., Stripping of Hazardous Chemicals from Surface Aerated Waste Treatment Basins. APCA/WPCF Specialty Conference on Control of Specific (Toxic) Pollutants, Gainesville, Florida, February 13-16 (1979).

Freeman, R. A., J. M. Schroy, J. R. Klieve, and S. R. Archer, Experimental Studies on the Rate of Air Stripping of Hazardous Chemicals from Waste Treatment Systems," 73rd APCA Meeting, Montreal, Canada, June 22-27, 1980a. Paper No. 80-16.7.

Freeman, R. A., Laboratory Study of Biological System Kinetics, unpublished by Catalytic, Inc. under contract with EPA, 1980b.

Freeman, R. A., Comparison of Secondary Emissions from Aerated Treatment Systems, presented at the 1982 Winter AIChE National Meeting, Orlando, Florida, March 3, 1982. Paper No. 5c.

Gerber, V. Y., V. M. Sharafutdinov and A. Ya. Gerceridov, Kinetics of Biochemical Oxidation of Refinery Wastewaters, Chem. Technol. Fuels Oils (USSR) *12*: 826 (1976).

German Society for Petroleum Science and Carbon Chemistry (DGMK) and the Federal Ministry of the Interior (BMI). Measurement and Determination of Hydrocarbon Emissions in the Course of Storage and Transfer in Above- Ground Fixed Cover Tanks With and Without Floating Covers. BMI-DGMK Joint Projects 4590-10 and 4590-11; translated for EPA by Literature Research Company, Annandale, VA.

Grau, P., M. Dohanyos, and J. Chudoba, Kinetics of Multicomponent Substrate Removal by Activated Sludge, Water Research, Pergamon Press, Vol. 9, 637, 1975.

Hartley, G. S. Evaporation of Pesticides, published in Advances in Chemistry Series 86, American Chemical Society, Washington, D.C., 1969. pp. 115-134.

Hillenbrand, E., JRB Associates, McLean, VA, private communication based on the Draft Report, "Failure Incidents Analysis: Evaluation of Storage Failure Points," submitted to EPA Office of Solid Waste. March 1982.

Hwang, Seong T. Treatability and Pathways of Priority Pollutants in the Biological Wastewater Treatment. Paper presented at the American Institute of Chemical Engineers Symposium, Chicago, November 1980.

Hwang, S. T. Toxic Emissions from Land Disposal Facilities. *Environmental Progress*, Vol. I, No. 1. February 1982.

ICF, Inc., Clement Associates, Inc. and SCS Engineers, Inc., "RCRA Risk/Cost Policy Model Project," Phase 2 Report Submitted to EPA, Office of Solid Waste, June 15, 1982.

Kincannon, Donald F. and Enos L. Stover, Stripping Characteristics of Priority Pollutants During Biological Treatment. Paper presented at the Secondary Emissions Session of 74th Annual AICHE Meeting, New Orleans. November 1981.

Kincannon, Donald F., et al. Predicting Treatability of Multiple Organic Priority Pollutants in Wastewater from Single Pollutant Treatability Studies. Paper presented at the 37th Purdue Industrial Waste Conference, Purdue University, West Lafayette, Indiana. May 1982.

Lai, Sung-Ho, James M. Tiedje, and A. Earl Erickson. In situ Measurement of Gas Diffusion Coefficient in Soils. *Soil Science Society Proceedings*. 40. 1976.

Liss, P. S. and P. G. Slater. Flux of Gases Across the Air-Sea Interface. *Nature*, Vol. 247. January 1974.

Lyman, Warren J., William F. Rechl and David H. Rosenblatt, Handbook of Chemical Property Estimation Methods. McGraw-Hill, New York, 1982.

Mackay, Donald and Aaron W. Wolkoff. Rate of Evaporation of Low-Solubility Contaminants from Water Bodies to Atmosphere. *Environmental Science and Technology*, Vol. 7, No. 7. July 1973.

Mackay, Donald and Ronald S. Matsugu. Evaporization Rates of Liquid Hydrocarbon Spills on Land and Water. *Canadian Journal of Chemical Engineering*, Vol. 51. August 1973.

Mackay, Donald and Paul J. Leinonen. Rate of Evaporation of Low-Solubility Contaminants from Water Bodies to Atmosphere. *Environmental Science and Technology*, Vol. 9, No. 13. December 1975.

Mackay, Donald and T. K.Yuen. Volatilization Rates of Organic Contaminants from Rivers. *Water Pollution Journal of Canada*, Vol. 15, No. 2. Pergammon. 1980.

Mackay, Donald. Environmental and Laboratory Rates of Volatilization of Toxic Chemicals from Water. Hazard Assessment of Chemicals, Current Developments, Vol. 1. 1981.

Masser, Charles C. Compilation of Air Pollution Emission Factors, Supplement 12. U.S. Environmental Protection Agency. Research Triangle Park, NC, April 1981.

McCord, Andrew T. A. Study of the Emission Rate of Volatile Compounds from Lagoons, presented at the National Conference of Management of Uncontrolled Hazardous Waste Sites. Washington, D.C. October 28-30, 1981.

McDonald, Randy, EPA Office of Emission Standards Engineering Division, Research Triangle Park, NC, private communication with Ronald Bell, GCA/Technology Division, August 6, 1982.

Millington, R. J. and J. P. Quirk, Permeability of Porous Solids. Trans. Faraday Soc. 57:1200-1207, 1961.

Millington, R. J. and R. C. Shearer. Diffusion in Aggregated Porous Media, *Soil Science*. III. 1971.

Moryakov, U.S., et al. Losses of Crude Oil and Products in Operation of Refinery Storage Tanks. Translated from Khimiya i Tekhnologiya Toplivi i Masel, No. 4, pp. 8-10, April 1979.

Murphy, B. L., et al. Outer Continental Shelf Oil Spill Probability Assessment, Volume 2, Data Analysis Report. Submitted to U.S. Department of Interior, Bureau of Land Management, November 1981.

Neely, W. Brock. Predicting the Flux of Organics Across the Air/Water Interface. Proceedings of 1976 National Conference on Control of Hazardous Material Spills. New Orleans, LA. April 25-28, 1976.

Nelson, R. W., G. W. Gee, and D. W. Mayer. Control of Radon Emissions from Uranium, Mill Tailings by Multilayered Earth Barriers. Transcripts of American Nuclear Society, 38. 1981.

Owens, M., R. W. Edwards, and J. W. Gibbs. Some Reaeration Studies in Streams. International Journal of Air and Water Pollution, Vol. 8. Pergamon Press. 1964.

Patterson, J. W. and P. S. Kodukala. Biodegradation of Hazardous Organics Pollutants. Chemical Engineering Progress. April 1981.

Rolston, D. E. and B. D. Brown. Measurement of Soil Gaseous Diffusion Coefficients by a Transient-State Method with a Time-dependent Surface Condition. Soil Science Society American Journal, 40. 1976.

Shen, Thomas T. Emission Estimation of Hazardous Organic Compounds from Waste Disposal Sites. Presented at the 73rd Annual Meeting of the Air Pollution Control Association. Montreal, Quebec. June 22-27, 1980.

Shen, Thomas T. Estimating Hazardous Air Emissions from Disposal Sites. Pollution Engineering. August 1981.

Shen, Thomas T. Estimation of Organic Compound Emissions from Waste Lagoons. Journal of the Air Pollution Control Association, Vol. 32, No. 1. January 1982.

Smith, James H., David C. Bomberger Jr. and Daniel L. Haynes. Prediction of the Volatilization Rates of High-Volatility Chemicals from Natural Water Bodies, Environmental Science and Technology, Vol. 14, No. 11. November 1980.

Smith, James H., David C. Bomberger Jr. and Daniel L. Haynes. Volatilization Rates of Intermediate and Low Volatility Chemicals from Water. Chemosphere, Vol. 10, No. 3. 1981.

Springer, Charles, University of Arkansas, Fayetteville, Arkansas, private communication with William Farino, GCA/Technology Division. January 17, 1983.

Steenhuis, T. S., G. D. Bubenzer and J. C. Converse. Ammonia Volatilization of Winter Spread Manure. Transactions of the ASAE, 1979. pp. 152-161.

Sutton, O. G., Micrometerology, McGraw-Hill, New York, 1953.

Taylor, Sterling A. Oxygen Diffusion in Porous Media as a Measure of Soil Aeration, Soil Science Society Proceedings, 14, 55-61. 1949.

Thibodeaux, L. J. and D. G. Parker, "Desorption Limits of Selected Industrial Gases and Liquids from Aerated Basins," paper No. 30d, 76th National Meeting, AIChE, Tulsa, OK. March 1974.

Thibodeaux, L. J., "Air Stripping of Organics from Wastewater: A Compendium," Proceedings of the Second National Conference on Complete Water Use, Chicago, Illinois. May 4-8, 1978.

Thibodeaux, L. J., Chemodynamics: Environmental Movement of Chemicals in Air, Water, and Soil. John Wiley & Sons, New York, 1979.

Thibodeaux, L. J. Estimating the Air Emissions of Chemical from Hazardous Waste Landfills. Journal of Hazardous Materials 4 (1981a). 235-244.

Thibodeaux, L. J., Charles Springer, and Lee M. Riley. Models of Mechanisms for the Vapor Phase Emission of Hazardous Chemicals from Landfills, presented at Symposium of Toxic Substances Management, Atlanta, GA. March 1981b.

Thibodeaux, L. J., D. G. Parker, H. H. Heck and R. Dickerson. Quantifying Organic Emission Rates from Surface Impoundments with Micrometeorological and Concentration Profile Measurements, for presentation at the annual meeting of American Institute of Chemical Engineers. New Orleans, LA. November 8-12, 1981c.

Thibodeaux, L. J., David G. Parker and Howell H. Heck. Measurement of Volatile Chemical Emissions from Wastewater Basins. USEPA-IERL. December 1981d.

Thibodeaux, L. J. and S. T. Hwang. Landfarming of Petroleum Wastes - Modeling the Air Emission Problem. Environmental Progress, Vol. I, No. 1. February 1982a.

Thibodeaux, L. J., C. Springer, T. Hedden, and P. Lunney. Chemical Volatilization Mechanisms from Surface Impoundments in the Absence of Wind. Land Disposal of Hazardous Waste, EPA-600/9-82-002. March 1982b.

Thibodeaux, L. J., C. Springer, P. Lunney, S. C. James and T. T. Shen, Air Emission Monitoring and Hazardous Waste Sites, Proceedings of 3rd National Conference on Management of Uncontrolled Hazardous Waste Sites, November 29 to December 1, 1982c.

Towell, G. C., G. P. Strand and G. H. Ackerman, "Mixing and Mass Transfer in Large Diameter Bubble Columns," AICHE-I, Chem. Eng. Symposium Series No. 10, London: Inst. Chem. Eng., page 10-97, 1965.

TRW Environmental, Inc., Background Documentation for Storage of Organic Liquids. EPA Contract No. 68-02-3174, May 1981.

U.S. Environmental Protection Agency. Emission Test Report-Breathing Loss emissions from Fixed-Roof Petrochemical Storage Tanks. EMB 78-OCM-5, Research Triangle Park, NC, February 1979.

Western Oil and Gas Association. Hydrocarbon Emissions from Fixed-Roof Petroleum Tanks. Prepared by Engineering-Science, Inc., Los Angeles, CA, July 1977.

Wukash, R. F., C. P. Grady and E. J. Kirsch. Prediction of the Fate of Organic Compounds in Biological Wastewater Treatment Systems. AIChe Symposium, Water-1980, pp. 137-143, 1981.

APPENDIX B

DERIVATION OF CURRIE WET SOIL CORRELATION FOR EFFECTIVE DIFFUSIVITY

CURRIE (1960) DRY SOIL CORRELATION

$$\frac{D}{D_o} = \gamma\ \varepsilon^{\mu}$$

where D = diffusion coefficient in dry soil;

D_o = air diffusion coefficient;

ε = soil porosity;

γ, μ = constants for a specific type of soil.

CURRIE (1961) WET SOIL CORRELATION

$$\frac{D}{D_v} = \left(\frac{\varepsilon_a}{\varepsilon_v}\right)^{\sigma}$$

where D = diffusion coefficient in wet soil;

D_v = diffusion coefficient in air-filled soil;

ε_a = air-filled soil porosity;

ε_v = inter-crumb pore spaces;

σ = soil specific constant.

Derive D_v:

for dry soils, $\varepsilon_a = \varepsilon_T$

where ε_T = total porosity

$$D = D_o\ \gamma\ \varepsilon^{\mu} = D_o\ \gamma\ \varepsilon_T{}^{\mu}$$

$$D = D_v \left(\frac{\varepsilon_a}{\varepsilon_v}\right)^{\sigma} = D_v\left(\frac{\varepsilon_T}{\varepsilon_v}\right)^{\sigma}$$

$$D_v = D_o \gamma \varepsilon_T{}^{\mu} \left(\frac{\varepsilon_v}{\varepsilon_T}\right)^{\sigma}$$

substituting D_v into wet soil correlation;

$$D = D_v \left(\frac{\varepsilon_a}{\varepsilon_v}\right)^{\sigma} = D_o \gamma \varepsilon_T{}^{\mu} \left(\frac{\varepsilon_v}{\varepsilon_T}\right)^{\sigma} \left(\frac{\varepsilon_a}{\varepsilon_v}\right)^{\sigma}$$

$$D = D_o \gamma (\varepsilon_T)^{\mu-\sigma} (\varepsilon_a)^{\sigma}$$

check for dry soil, $\varepsilon_a = \varepsilon_T$

$$D = D_o \gamma \varepsilon_T{}^{\mu}$$

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16. ABSTRACT

Mathematical models describing the release rate of volatile air emissions from hazardous waste treatment, storage, and disposal facilities were compiled and reviewed. Mathematical modeling techniques which predict volatile air emissions release rates from landfills, landfarms, surface impoundments, storage tanks, wastewater treatment processes, and drum handling and storage facilities were assessed. Existing field test validation efforts were also reviewed.

The purpose of this report is to provide a source of current information available on this subject area. A guidance manual of practice will ultimately be prepared to assist regulatory engineers and others in applying the recommended models. Since many new papers in this area are continually being published, this selection of modeling techniques may be considered present state-of-the-art as of spring 1983. Field validation scheduled to be conducted in 1983 and 1984 under EPA and private directives should provide additional information regarding model precision.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Air Pollution Pollution Control Hazardous Waste TSDF Volatile Organic Compounds (VOC) Air Emission Models	Air Pollution Control	

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22. PRICE